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Experimental Engineering Support for EPA's FBC Program: Final Report
Volume III. Solid Residue Study

Westinghouse Research and Development Center
Pittsburgh, PA

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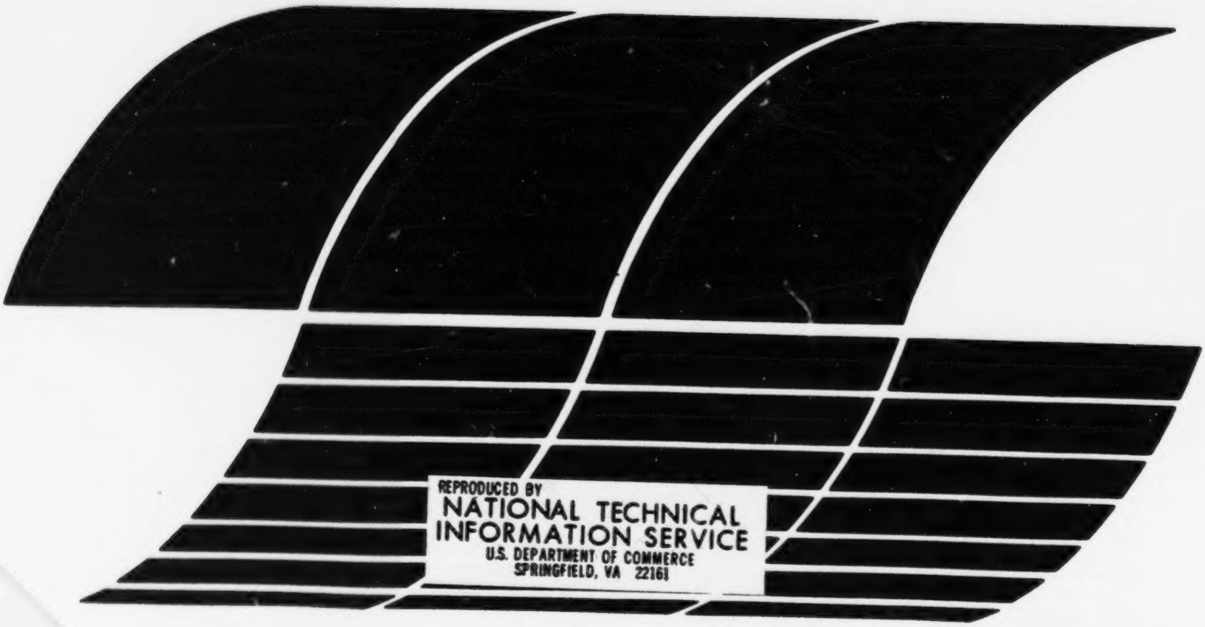

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16. ABSTRACT The report gives results of experimental studies of the leaching properties and thermal activity of solid residues from the fluidized-bed combustion (FBC) of coal. Means for processing the residues, to reduce the environmental impact of their disposal, are also studied. Previous leaching and thermal activity tests were expanded to include residues from additional experimental FBC units, including both atmospheric and pressurized systems. Leaching tests were conducted on both untreated residues and residue samples processed into a cement-like material. Results indicate that the major potential contaminants in the leachate from the FBC residues are the high pH, total dissolved solids, and sulfate levels, all of which are above drinking water regulations. Heat release when initially exposed to water, due to calcium oxide hydration, may also create a handling problem. Trace metals in the leachate do not generally exceed drinking water regulations. Processing of the residues caused some reduction in leachate contaminant levels. Additional tests on processing and utilizing FBC residues are also reported.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Metals	Pollution Control	13B	07B
Combustion	Waste Treatment	Stationary Sources	21B	
Fluidized Bed Processing		Thermal Activity	13H,07A	
Coal		Trace Metals	21D	
Residues				
Leaching			07D	

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PREFACE

The Westinghouse R&D Center is carrying out a program to provide experimental and engineering support for the development of fluidized-bed combustion systems under contract to the Industrial Environmental Research Laboratory (IERL), U.S. Environmental Protection Agency (EPA), at Research Triangle Park, NC. The contract scope includes atmospheric (AFBC) and pressurized (PFBC) fluidized-bed combustion processes as they may be applied for steam generation, electric power generation, or process heat. Specific tasks include work on calcium-based sulfur removal systems (e.g., sorption kinetics, regeneration, attrition, modeling), alternative sulfur sorbents, nitrogen oxide (NO_x) emissions, particulate emissions and control, trace element emissions and control, spent sorbent and ash disposal, and systems evaluation (e.g., impact of new source performance standards (NSPS) on FBC system design and cost).

This report contains the results of work defined and completed under the spent sorbent and ash disposal task of the contract. Work on this task was performed from January 1976 to January 1979 and is documented in the following contract reports:

- "Disposal of Solid Residue from Fluidized-Bed Combustion: Engineering and Laboratory Studies," EPA-600/7-78-049 (NTIS PB 283-082), issued in March 1978, which presented the results of work performed from January 1976 to January 1977
- The present report, which presents the results of extended environmental impact tests, comparisons with reference materials, and screening tests and analyses on the potential for processing FBC residue for disposal or utilization. The report documents work performed from January 1977 to January 1979 and subsequent extensions from review of the draft through October 1979.

Since proper disposal of solid residue is of primary importance to the commercialization of the FBC process, continuing effort is directed toward solid residue studies under the current Westinghouse contract to EPA (68-02-3110).

Work on the other tasks performed under this contract has also been reported:

- Experimental/Engineering Support for EPA's FBC Program: Final Report Volume 1, Sulfur Oxide Control, EPA-600/7-80-015a, January 1980.
- Experimental/Engineering Support for EPA's FBC Program: Final Report Volume II, Particulate, Nitrogen Oxide, and Trace Element Control, EPA-600/7-80-015b, January 1980.
- Experimental/Engineering Support for EPA's FBC Program: Final Report Volume IV, Engineering Studies, EPA-600/7-80-015d, January 1980.
- Effect of SO_2 Emission Requirements on Fluidized-Bed Combustion Systems: Preliminary Technical/Economic Assessment, EPA-600/7-78-163, August 1978.
- Regeneration of Calcium-Based SO_2 Sorbents for Fluidized-Bed Combustion: Engineering Evaluation, EPA-600/7-78-039, NTIS PB 281-317, March 1978.
- Alternatives to Calcium-Based SO_2 Sorbents for Fluidized-Bed Combustion: Conceptual Evaluation, EPA-600/7-78-005, January 1978.
- Evaluation of Trace Element Release from Fluidized-Bed Combustion Systems, EPA-600/7-78-050, NTIS PB 281-321, March 1978.

ABSTRACT

Partially reacted limestone or dolomite and coal ash from atmospheric and pressurized fluidized-bed combustion systems must be disposed of or utilized in an environmentally acceptable manner. A preliminary understanding of the environmental impact of the disposal of the solid residue and perspective on selected choices available for direct disposal and residue processing for utilization or disposal have been developed. Laboratory testing programs have been developed to determine the chemical and physical characterization, leaching behavior, and residual activity of FBC solid residues. Processing of FBC solid waste (bed overflow and carry-over material) has been studied to investigate the potential for reducing environmental impact and to provide for potential utilization. The impact of environmental legislation and regulations is assessed, with particular emphasis on the regulations to be promulgated under the Resource Conservation and Recovery Act (RCRA, 1976). The environmental impact of the disposal of processed and unprocessed FBC sorbent is projected and compared with natural gypsum and FGD spent materials.

Environmental complications associated with the disposal of FBC solid waste are not likely to limit the development of FBC processes, and the solid residues are judged to be nonhazardous* materials under the classifications of proposed RCRA regulations. Processing techniques based on compaction of FBC solid waste may provide environmentally improved or utilizable waste products.

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*Nonhazardous is used in this report to identify a solid that does not qualify as hazardous under RCRA. It does not imply an absence of environmental impact.

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NOMENCLATURE

AFBC - atmospheric pressure fluidized-bed combustion
ANL - Argonne National Laboratory
B&W - Babcock and Wilcox Company
CAFB - chemically active fluidized bed
Ca/S - calcium-to-sulfur ratio
CBC - carbon burnup cell
CSO - Columbus Southern Ohio Company
DOE - Department of Energy
DWS - Drinking Water Standards
EDAX - energy dispersive analysis by X-ray
EMA - electron microprobe analysis
EP - extraction procedure
EPA - Environmental Protection Agency
EPRI - Electric Power Research Institute
ESP - Electrostatic Precipitator
FBC - fluidized-bed combustion
FGD - flue gas desulfurization
GE - General Electric Corporation
IERL/RTP - Industrial and Environmental Research Laboratory, Research Triangle Park, NC
LGE - Louisville Gas and Electric Company
MERC - Morgantown Energy Research Center
NIPDWR - National Interim Primary Drinking Water Regulations
PER - Pope, Evans and Robbins
PFBC - pressurized fluidized-bed combustion
RCRA - Resource Conservation and Recovery Act of 1976
SEM - scanning electron microscopy
SFA - sintered fly ash

NOMENCLATURE (Continued)

SBM - spent bed material
TDS - total dissolved solids
TEP - toxic extraction procedure
TGA - thermogravimetric analysis
TOC - total organic carbon
USPHS - U. S. Public Health Service
WHO - World Health Organization

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1. INTRODUCTION

Fluidized-bed combustion (FBC) for electric power generation, when compared with conventional technology, provides the potential for improved thermal conversion efficiency, reduced costs, and reduced environmental impact. The fluidized-bed combustion process, operated at atmospheric (AFBC) or elevated pressure (PFBC), typically results in the production of dry, partially utilized dolomite or limestone particles from 0 to 6 mm in size. In addition, fine particles of sorbent and ash are collected in the particulate-removal system. The sorbent material may be either regenerated for recycling to the fluid-bed boiler for repeated sulfur dioxide (SO_2) removal or disposed of in its partially sulfated form in a once-through system. The properties of these spent sorbents (size distribution, composition, etc.) depend on the FBC operating and design parameters. The major compounds in the waste stone to be disposed of are calcium sulfate ($CaSO_4$), calcium oxide (CaO), calcium carbonate ($CaCO_3$), and magnesium oxide (MgO), when dolomite is used; and $CaSO_4$ and CaO or $CaCO_3$ when limestone is used. Trace elements arising from impurities in the coal and sorbent will also be present.

The quantity of spent sorbent will depend on the sulfur content of the fuel, the emission standard, the operating conditions, and the sorbent characteristics. The spent sorbent for disposal will generally range from 0.01 to 0.5 kg sorbent/kg coal. Disposal of the coal ash is also considered.

The environmental acceptability of FBC residue disposal is dictated by the constraints of environmental laws and regulations. The three primary environmental laws are the Resource Conservation and Recovery Act (RCRA) of 1976 (the Solid Waste Disposal Act of 1965, as amended by

P. L. 94-580, 1976),[1] the Federal Water Pollution Control Act of 1972 (Public Law 92-500, 1972, as amended by Clean Water Act, P. L. 95-217, 1977),[2,3] and the Clean Air Act Amendments, 1977 (Clean Air Act, 1970 as amended).[4] The passage of RCRA closed the legislative loop of environmental laws (air/water/solid) and created a new level of control over solid waste disposal. The regulations to be promulgated under RCRA Subtitle C and Subtitle D on hazardous and nonhazardous waste disposal will have the greatest impact on FBC residue disposal.

An understanding of the environmental impact of the disposal or use of the spent sorbent and fly ash is critical to the successful implementation of FBC processes. This investigation is designed to provide a basis for projecting the environmental impact of disposal, interpreting results from large-scale demonstration sites, screening utilization options in view of the environmental impact, and developing optimal system design and operating requirements to minimize the environmental impact of the spent sorbent and coal ash. The scope of the program conceived to achieve these objectives includes identification of FBC spent sorbent and coal ash characteristics and quantities, development of laboratory tests to quantify the environmental impact of disposal, conducting environmental impact tests on actual FBC spent sorbent and ash, and performing studies to investigate potential processing options and their environmental impact.

An assessment of the potential environmental impact and a perspective on the potential for direct disposal and for processing for disposal or utilization are presented. Since proper disposal of solid residue is of primary importance to the commercialization of the FBC process, continuing effort is directed toward solid residue studies under the Westinghouse current contract to EPA (68-02-3110).

Two reports are being prepared that will present the results of FBC solid residue leachate characteristic determination using the RCRA test procedures and the results of an evaluation of methods for disposal of FBC residues.

2. SUMMARY AND CONCLUSIONS

The FBC solid residue studies reported here cover two major topics:

- Environmental impact. Experimental studies were carried out to investigate the environmental impact of direct disposal of dry FBC residues and of disposal after processing.
- Residue processing. Experimental engineering studies were conducted to evaluate residue processing options for utilization or for reducing environmental impact.

Results from these and related studies lead to the following conclusions:

- FBC residue disposal will not be an obstacle to commercialization of FBC systems.
- FBC residues tested would not constitute a hazardous waste based on RCRA criteria.
- Potential concerns for the disposal of FBC residue are the quantity; the chemical impact of calcium (Ca), sulfate (SO_4), dissolved solids (TDS), and pH; and the thermal activity under specific operating conditions.
- Low-temperature processing of FBC residue can reduce its environmental impact. Stable compacts have been formed and tested, showing that fixation reduces both the rate of leaching and the concentration of solutes.
- Low-temperature processing offers the potential for producing material applicable for use as aggregate.
- Options ranging from direct disposal to fixation are available for meeting specific applications, site requirements, and environmental impact constraints.

ASSESSMENT OF ENVIRONMENTAL IMPACT

The work accomplished in this area includes the following:

- Comprehensive testing encompassing three major areas:
    - Residue characterization
    - Leaching property
    - Thermal activity
- Development and use of screening tests to investigate leaching and thermal properties
- Testing of over 30 samples of FBC solids covering a wide range of FBC process variations:
    - FBC units: Exxon miniplant PFBC (once through and regenerative)
      Argonne National Laboratory (ANL) PFBC
      Combustion Power PFBC, adiabatic
      Pope, Evans and Robbins (PER) AFBC
      Babcock and Wilcox (B&W) AFBC
      Battelle - Columbus Laboratories AFBC
      Morgantown Energy Research Center (MERC) AFBC
    - FBC system: AFBC/PFBC/adiabatic; once through/regenerative
    - Residue source: spent bed material and carry-over (primary, secondary, and tertiary flue gas particle collectors)
    - Fuel: six sources of coal
    - Sorbent: five limestones and four dolomites
    - Operating conditions: T = 600 to 1000°C
      P = 101.3 to 1013 kPa (1 to 10 atm)
      Ca/S = 0.5 to 4
- Environmental impact of both direct disposal of FBC residue and disposal after further processing
- Conventional power plant residues (fixed and unfixed FGD sludge) and natural gypsum tested to provide perspective and comparison

- Preliminary investigation of leaching property as a function of leaching media (deionized water, CO_2-saturated water, and acidic acetate buffer)
- Review of legislative and regulatory constraints, in particular, The Resource Conservation and Recovery Act (RCRA),[1] as they are related to FBC residue disposal
- Assessment of the potential environmental impact of FBC residue disposal and the identification of major concerns.

Table 1 summarizes the results from the comprehensive test program. Conclusions based on these results are that:

- The potential concerns with FBC residue disposal are the pH, the TDS, calcium and (SO_4) in the leachate, its thermal activity, and the quantity of solid to be disposed of for some sites.
- The leachability and the thermal activity can be effectively reduced by further processing.
- The trace elements and total organic carbon (TOC) in leachates are extremely low in the leachate of both the unprocessed and the processed FBC residue and are not expected to be a problem.
- The leachate of the FBC carry-over has, on the average, lower pH, calcium, and TDS, but higher trace elements than does the leachate of bed material.
- Thermal activity is largely dependent on the amount of CaO present in the residue and is a function of the operating conditions, resulting in either calcined or uncalcined sorbent in the form of CaO or $CaCO_3$, respectively.
- Thermal activity is higher in the AFBC than in the PFBC residues tested, higher in bed material than in the carry-over.
- The leachate of AFBC residue with limestone sorbent averages higher pH, calcium, and TDS than does that of PFBC with dolomite sorbent.

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Table 1

COMPARISON OF ENVIRONMENTAL CONCERNS

Process	FBC		FGD[b]			Natural Gypsum
Parameter	Unprocessed	Processed	Unprocessed	Oxidized	Stabilized	Unprocessed
Hazardous Characteristics[a]	no	no	no	no	no	no
Leachate Characteristics						
Trace Elements			X	X		
Total Organic Carbon						
pH	X	c				
TDS	X	c	X	X	X	X
Ca	X	c	X	X	X	X
Mg			X	X	X	
Sulfate	X	c	X	X	X	X
Sulfite			X			
Sulfide	d					
Thermal Activity	yes[e]	no	no	no	no	no
Physical Strength	no	no	yes	no	no	no
Quantity	yes	yes	yes	yes	yes	Not applicable

X = Exceeds DWS where they exist.

[a] Detailed report on test data will be issued later in 1980.

[b] Limited to lime or limestone scrubber sludge.

[c] Leachability significantly reduced, degree of improvement depending on processing alternatives.

[d] Not a concern for the once-through FBC residue; further investigation needed for spent sorbent with sorbent regeneration.

[e] Associated with residue with a substantial amount of unutilized CaO, e.g. AFBC bed material.

- Leaching property is a function of the pH of the leaching medium. Trace elements in leachate, in general, increase with decreasing pH.
- Although an absolute comparison may not be possible, general trends have shown that the physical, chemical, and leaching properties of FBC residue are superior to the nonstabilized FGD sludge with regard to disposal and are comparable to the chemically and physically stabilized FGD residue from the conventional power plant.
- On the basis of the proposed regulations and identification methods for hazardous waste under RCRA Sec. 3001 and the FBC residue characteristics reported here, we expect FBC residue to be nonhazardous. Further work is being carried out under Westinghouse's current contract with EPA and will be discussed in a separate report.
- In summary, based on the findings reported here and in previous Westinghouse reports,[5,6] we expect that disposal of FBC residue will not be a problem in the commercialization of the FBC process.

SPENT SORBENT PROCESSING

We have reported processing alternatives previously[5,6] and have demonstrated that stable, solid compacts could be produced from blends of FBC spent sorbent and coal ash at ambient temperature and pressure. The work reported here on spent sorbent processing presents a preliminary engineering assessment of fixation into compacts as a means of protecting the environment, data on the potential long-term stability of compacts, and an assessment of the possibility of using the residues directly as aggregate or concretes.

An assessment of the potential for reducing the enviromental impact of FBC residues by processing them at low temperature into compacts was carried out on the basis of leachate results from unprocessed and processed materials. Calcium leached was used to represent leaching characteristics. Results show:

- Batch leaching behavior for 5-cm cubes made from blends of spent bed material and carry-over can be predicted at least to 1080 hours by an empirical relation of the form

  $$L_T = L_0 \left(1 - e^{-b_1 N}\right) + b_2 N \quad ,$$

  where

  L_T = cumulative calcium leached, mg-moles
  N = number of 72-hr extraction, and L_0, b_1, b_2 are constants.

- For large masses the leaching rate/m^2 of exposed surface is more meaningful than the rate/g. For such masses the amount of material leached is constrained by the amount of local precipitation. Leaching of major constituents (Ca^{++}, $SO_4^{=}$, OH^-) from such masses includes an initial transient that in most situations will probably not be an environmental problem.
- Processing FBC residues to 5-cm cubes reduced the leaching rate of calcium/g of sample by a factor of 5.
- The concentration of leachates will be unsaturated and below 10 times the drinking water standard (10 x DWS) for unprocessed and processed material, with the time for complete solution of residue from a 200 MW plant requiring >3000 years.

A freeze-thaw test was selected to provide a screening test for stability. The current effort did not permit a comprehensive investigation, and, thus, only isostatically pressed compacts were used to provide an estimate of limiting performance capability. Specimens were made from ground spent sorbent and were subjected to 300 cycles of freeze-thaw exposure at -18 to +4°C. Results show:

- Spent bed material from the FBC of bituminous coal can be processed to large masses that are resistant to degradation by freeze-thaw cycling.
- Mixtures of spent bed material and carry-over may have to be preslaked either separately or jointly in order to achieve the same results indicated above.
- Further work is needed to identify the nature of the bond in the processed spent bed material.

Utilization of FBC residue directly as an aggregate was investigated. Results show:

- Spent bed material containing up to 39 wt % total CaO can be used as fine aggregate in conjunction with sintered fly ash to make concrete mortar with a compressive strength in the range of normal concrete.
- Briquetting of FBC residue has the potential for use as an aggregate.

3. RECOMMENDATIONS

The FBC residue studies were initiated in 1974 and subsequently expanded into the current comprehensive program encompassing two major areas:

- The environmental impact assessment of direct disposal and disposal after further processing
- Residue processing for disposal and for utilization.

ASSESSMENT OF ENVIRONMENTAL IMPACT

An understanding of the environmental impact of residue disposal is critical to the successful commercialization of the FBC process. Based on the studies reported in this and previous Westinghouse reports, further investigations are recommended:

- The impact of RCRA should be fully understood. An understanding of the impact of future regulations such as the radioactivity and bioaccumulation characteristics stated in the Advance Notice in the Federal Register (December 18, 1979) for hazardous waste should be developed. Standards and guidelines for hazardous and nonhazardous waste disposal facilities to be promulgated under RCRA Sections 3004 and 4004, respectively, deserve special attention because of their potential economic impact on solid residue disposal.
- Laboratory-scale screening of residue disposal should continue in order to determine environmental impact as a function of process variations and to fill gaps in the data, in particular by using residues from those systems from which representative samples were unavailable during this study. Examples of these system variations are FBC

with sorbent regeneration, adiabatic PFBC operation, and residue from FBC using western coals. In addition, the carry-over fines collected after the secondary cyclone require further study since some trace elements have appeared in the leachates from such materials at levels exceeding the DWS.

- A methodology should be developed to evaluate the environmental impact of disposal at specific sites based on the site-specific hydrology, geology, climate, and soil compositions. Such methodology will simplify the site-selection and disposal facility design tasks.
- Perspective should be provided on the role of leachate attenuation by soil or other disposal media.
- The effect of acidic leaching medium is recommended for further investigation.
- The potential advantages and disadvantages of codisposal of FBC waste, which is highly alkaline, with acidic waste, such as coal-cleaning waste, should be assessed.
- A systematic engineering evaluation of the alternative methods of handling and disposing of the FBC residue is required to provide a basis for making the optimal economic choice and for meeting the environmental criteria.
- The environmental impact of processed FBC residue should be investigated further as improved and/or additional processing or utilization options are developed.

SPENT SORBENT PROCESSING

An understanding of spent sorbent processing is important for developing an understanding of the choices available for minimizing the environmental impact of disposal and for utilizing the residue to achieve optimal resource recovery or economic benefit. Specific areas require further study:

- Analysis of environmental impact reduction using low-temperature compacts should be extended to improve the ability to relate test results to disposal site conditions.
- The long-term stability tests should be extended to include additional FBC residue characteristics (e.g., fines, coal source, etc.) to incorporate other criteria (e.g., autoclave expansion and sulfate resistance), and to include alternative low-temperature processed materials (e.g., compacts formed without pressing).
- The development work on utilization of residue as an aggregate should be extended to assess the impact of residue characteristics (e.g., fines concentration), to understand the mechanism of bonding responsible in compacts for the unusually high compressive strengths, and to implement further tests that would permit commercial utilization of FBC residue as an aggregate (e.g., abrasion resistance and concrete cylinder tests).

4. ENVIRONMENTAL CONSTRAINTS

The environmental acceptability of FBC residue disposal is dictrated by the constraints of environmental laws and regulations. This section reviews the federal laws and regulations as well as the criteria selected for this investigation.

REGULATIONS/CRITERIA

The federal laws having legislative power over the environmental impact of solid waste disposal are:

- Resource Conservation and Recovery Act (RCRA), 1976[1]
    - Solid Waste Disposal Act, 1965
    - Resource Recovery Act, 1970
- Clean Water Act, 1977[2]
    - Federal Water Pollution Control Act, 1972[3]
    - Safe Drinking Water Act, 1974
- Clean Air Act Amendments, 1977[4]
    - Clean Air Act, 1970
- Toxic Substances Control Act (TSCA), 1977
- Occupational Safety and Health Act (OSHA), 1970
- Marine Protection, Research and Sanctuaries Act, 1972.

Of the above, those that most affect solid waste disposal are RCRA[1] and the Federal Water Pollution Control Act of 1972 (Public Law 92-500, 1972, as amended by Clean Water Act, P.L. 95-217, 1977).[2,3] Eventually, disposal guidelines are to be promulgated by EPA under the authority of the former.

The passage of RCRA closed the legislative loop of environmental laws (air/water/solid) and created a new level of control over solid waste disposal. Of special concern are the regulations to be promulgated under Subtitle C - Hazardous Waste Management[7-9] and Subtitle D - State and Regional Solid Waste Plans.[10]

On December 18, 1978, EPA issued in the Federal Register[9] the proposed rules under RCRA Section 3001 (identification and listing of hazardous waste), Section 3002 (standards applicable to generators of hazardous waste), and Section 3004 (standards applicable to owners and operators of hazardous waste treatment, storage, or disposal facilities). These proposals, together with those already published pursuant to Section 3003 (standards applicable to transporters of hazardous waste, April 28, 1978, 43 FR 18506-18512), Section 3006 (authorized state hazardous waste programs, February 1, 1978, 43 FR 4336-4373), Section 3008 (federal enforcement, August 4, 1978, 43 FR 34738-34747), and Section 3010 (effective date, July 11, 1978, 43 FR 29908-29918) and that of the Department of Transportation pursuant to the Hazardous Materials Transportation Act (May 25, 1978, 43 FR 22626-22634), along with Section 3005 (permits for treatment, storage, or disposal of hazardous waste), constitute the hazardous waste regulatory program under Subtitle C of the Act.

According to the proposed rules under RCRA Section 3001, those characteristics that identify a waste as hazardous are its ignitability, corrosivity, reactivity, and toxicity. Also proposed in the same publication is the "Advance Notice for Proposed Rulemaking" which requests information and comments on the additional characteristics being considered for identifying hazardous waste -- radioactivity, genetic activity, bioaccumulation, and additional aspects of toxicity. A set of tests was proposed for each of the above hazardous characteristics. Among them the test for toxicity (extraction procedure, EP) received the most attention and was most relevant to FBC residue disposal. Tables 2 and 3 summarize the development of this procedure.

Table 2

DEVELOPMENT OF RCRA 3001 REGULATION

Draft Regulations	Proposed Regulations	Key Issues	Westinghouse Actions
March 1978		Toxic Extraction Procedure (TEP), drafted for hazardous waste identification	TEP initiated on selected samples • to assist RCRA Sec. 3001 development • to provide initial indication of "hazardous" or "non-hazardous" nature of residues.
Sept. 1978		TEP significantly modified, to be renamed extraction procedure, EP	
Nov. 1978	Dec. 18, 1978	• Extraction Procedure (EP) proposed - significantly different from the previous TEP • A structural integrity test (SIT) specified for monolithic block. • "Special Waste" Category created (including utility waste): subject to partial exemption of hazardous waste regulations. • Advance notice of Proposed Rulemaking on radioactivity and bioassay	EP initiated on selected FBC reference materials and raw sorbents.

Table 3

DEVELOPMENT OF EPA LEACH TEST

Parameters	Draft Date		Proposed in Fed. Reg.
	March 1978	Sept. 1978	Dec. 18, 1978
Sample Size	Not specified	$\geq$ 100 g	$\geq$ 100 g
Sample Preparation	Grinding to 3/8 in.	Grinding to 3/8 in., or SIT hammer test on monolithic block	Same as Sept. 1978
Leaching Medium	Deionized water with NaOH or acetic acid added	Deionized water with 0.5N acetic acid added	Same as Sept. 1978
Titrating Agent	1N NaOH or 1:1 acetic acid	0.5N acetic acid	Same as Sept. 1978
Maximum Titration	No Limit	Maximum = 4 ml/g solid	Same as Sept. 1978
Final pH	4.9-5.2	4.9-5.2 or controlled by maximum acid allowed	Same as Sept. 1978
Temperature	Room temperature	20-30°C	20-40°C
Extraction Time	2 x 24 hr = 48 hr total	24 hr Single extraction	Same as Sept. 1978
Solid/Liquid Ratio	1:10 for each extraction, plus original liquor	1:20 plus original liquor	Same as Sept. 1978
Agitator	Not specified	Not specified, but overhead stirring suggested	Same as Sept. 1978

Also under the proposed rules of RCRA Sec. 3001, there are two mechanisms by which to identify a waste as hazardous:

- Inclusion of the substance on the predetermined hazardous waste list of processes and sources
- Failure of the substance to meet the proposed test criteria for any of the identified hazardous characteristics.

FBC residue is not on the list. Should the identifying tests determine it to be hazardous (and preliminary results indicated that it would not be), in all likelihood it would be classified as a "special waste" and be subjected to partial exemption of RCRA Subtitle C - hazardous waste regulations. Should testing determine FBC residue to be nonhazardous, (as is predicted), the disposal would be subject to the "Proposed Classification Criteria for Solid Waste Disposal Facilities" under RCRA Sec. 4004[10] and the "Proposed Guidelines for Landfill Disposal of Solid Waste" under RCRA Sec. 1008.[11]

In addition to any controls that may be imposed upon FBC residue in connection with RCRA, some requirements may also result from the Federal Water Pollution Control Act (amended as the Clean Water Act, 1977).[2,3] The primary environmental concern with solid waste disposal is the potential ground and surface water contamination caused by leachate runoff or seepage. The federal regulation that most nearly relates to a limit on seepage water quality is the EPA's "Alternative Waste Management Techniques for Best Practical Waste Treatment"[12] under the authority of the Federal Water Pollution Control Act of 1972[3] amended by the Clean Water Act of 1977.[2] These criteria state that the contaminant levels in the groundwater under a disposal site shall be limited to the maximum contaminant levels contained in the National Interim Primary Drinking Water Regulations (NIPDWR)[13] or to the existing concentration if the latter is greater. If the groundwater is to be used for other than a drinking water supply, the groundwater criteria should be established by the Regional Administrator.

Because of the wide variation in the characteristics of solid wastes in general, weather, soils, topography, groundwater from site to site, and nearby stream quality and flow characteristics, solid waste disposal permits are currently being awarded on a site-specific basis. Eventually, as a result of the RCRA, state regulations will apply, but these regulations will not be enacted until federal standards are promulgated. Depending on the actual site selected for disposal, the resultant water would have to meet the water quality criteria for the specific water use.[14] Furthermore, the success of a land disposal application depends, above all, on the design, construction, and operation of a specific disposal site based on the geology, hydrology, and meteorology of that particular site.

TEST PROGRAM CRITERIA

A series of laboratory leaching tests on FBC residue is reported here. In order to have some criteria that could be used to provide a preliminary indication of the potential acceptability of the observed leachates from these laboratory studies, Westinghouse decided to compare the observed leachate concentrations with available drinking water standards/guidelines/criteria. These drinking water standards include the NPIDWR,[13] United States Public Health Service (USPHS)[15] Drinking Water Standards, and the World Health Organization (WHO) Potable Water Standards.[16] In addition, although the guidelines for power plant effluents[17] developed by EPA are not applicable to the disposal of dry spent sorbent from the fluidized-bed combustion process, they are used as additional references in this investigation. Table 4 lists the selected water quality criteria for comparison of leachate.

One should note that the drinking water standards are used as the criteria for comparison in this investigation only in an effort to put data into perspective, in the absence of formal EPA guidelines; this approach should not be construed as suggesting that the leachate must necessarily meet drinking water standards. This use of the drinking

Table 4

SELECTED WATER QUALITY CRITERIA

Substance	Drinking Water Standards, mg/ℓ				Effluent Guidelines for Standards for Steam Electric Power Generation,[17] mg/ℓ
	NIPDWR[13]	USPHS[15]	WHO[16]		
			Highest Desirable Level	Maximum Permissible Level	
Ag	0.05	0.05			
As	0.05	0.05	0.05	0.05	
Ba	1.0	1.0			
Ca			75	200	
Cd	0.01	0.01	0.01	0.01	
Cr	0.05	0.05 (Cr^{+6})			0.2
Cu		1.0	0.05	1.5	1.0
Fe		0.3	0.1	1.0	1.0
Hg	0.002		0.001	0.001	
Mg			30	150	
Mn		0.05	0.05	0.5	
Ni		2.0			
Pb	0.05	0.05	0.1	0.1	
Se	0.01	0.01	0.01	0.01	
Sn		1.0			
Zn		5.0	5.0	15	1.0
SO_4		250	200	400	
Cl		250	200	600	
NO_3	10 (as N)	45	45	45	
F	1.4-2.4	1.7	1.7	1.7	
pH (pH unit)			7.0-8.5	6.5-9.2	6.0-9.0
TDS		500	500	1500	

water standards for the purposes of this study is conservative; it assumes that no attenuation or dilution of the leached contaminants will occur in the substrate beneath the disposal pile, or in the groundwater. By comparison, according to the extraction procedure proposed under Sec. 3001 of RCRA to determine whether a substance is to be considered hazardous due to toxicity, a criterion of ten times the NPIDWR is used; it assumes that the leachate will be diluted by a factor of 10 between the disposal pile and the receptor (e.g., a well tapping the groundwater).

Another leachate concentration goal available is the Multimedia Environmental Goals (MEG) being developed by EPA's Industrial Environmental Research Laboratory in the Research Triangle Park, N.C. (IERL-RTP).[18,19] These independent, very conservative goals are, in their simplest form, based upon relatively simple manipulation of available Threshold Limit Value (TLV) and Lethal Dose 50 (LD_{50}) data.

EFFECT OF RESIDUE PROCESSING

While it may be technologically simpler and economically less costly to dispose of FBC residues directly, there is reason to believe that some on-site processing can reduce the environmental impact. The objective of the processing may be to place the product in a suitable disposal site or to use the product in road construction, in cement block, in agriculture, or in other ways. In either case an assessment of the product's conformity to environmental regulations will be required.

5. FBC SOLID RESIDUES

There are two major sources of solid residue from an FBC system: spent bed material and carry-over. The former consists largely of spent limestones or dolomite sorbent (calcium sulfate [$CaSO_4$], calcium oxide [CaO], calcium carbonate [$CaCO_3$], magnesium oxide [MgO]); and the latter consists of finer particles of spent sorbent and coal ash carried out from the bed and removed by a particle control device, such as a cyclone.

RESIDUE CHARACTERISTICS

Residue characteristics were projected and compared with actual FBC solids in the previous EPA report.[5] The projected spent sorbent compositions for three basic fluidized-bed combustion concepts are summarized in Table 5.

The size distribution of spent sorbent from the bed will be similar to the sorbent feed size distribution. The spent sorbent fines appearing in the fly ash will depend upon sorbent attrition rate, bed elutriation rate, and fines recycle (if applied). Practically all the coal ash will be elutriated from the combustor. The quantity of sorbent fines is estimated to range from 0.25 to 1 times the coal ash content of the fly ash for a nominal 10 percent ash coal.

Table 6 summarizes the approximate distribution ranges of spent sorbent and coal ash in the different sources of FBC residue (bed, carry-over) investigated in this study. Table 7 summarizes the composition range of the spent calcium-based sorbent in these solids. The individual samples investigated during this study and their chemical compositions will be presented in greater detail in Section 6 of this report.

Table 5

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PROJECTED SPENT SORBENT COMPOSITIONS FROM THREE BASIC FBC SYSTEMS[14]

Process	Sorbent	$CaSO_4$	Spent Sorbent Composition, mole % (wt %)				
			CaS	CaO	$CaCO_3$	MgO	Balance
Atmospheric-Pressure FBC Once-through 100% load	Limestone	25 (43.7)	0 (0)	75 (54)	0 (0)	0[b] (0)	1.73[d] (2.3)
Pressurized Boiler Once-through 100% load	Dolomite	80 (64.1)	0 (0)	20 (6.6)	0 (0)	1.19[c] (28.1)	2.11[d] (1.2)
Adiabatic Combustor Once-through 100% load	Dolomite	50 (46.7)	0 (0)	50 (19.2)	0 (0)	1.19[c] (32.7)	2.11[d] (1.4)
Pressurized Boiler Once-through 100% load	Limestone	40 (60.6)	0 (0)	60 (37.4)	0 (0)	0[b] (0)	1.73[d] (2)
Atmospheric Pressure FBC One-step regeneration 100% load	Limestone	24[e]/12.8[f] (43.1/26.1)	0[e]/1.2[f] (0/1.3)	76[e]/86[f] (54.6/70.1)	0 (0)	0[b] (0)	1.73[d] (2.3/2.5)
Pressurized Boiler Once-through turndown to minimum load	Dolomite	60 (47.6)	0 (0)	0 (0)	40 (23.4)	1.19[c] (27.8)	2.11[d] (1.2)

[a] Basis: Limestone 1359, Dolomite 1337 and Ohio-Pgh No. 8 coal

[b] MgO included with balance of components

[c] Moles MgO/mole Ca

[d] Grams/mole calcium

[e] Spent sorbent from combustor

[f] Spent sorbent from regenerator

In addition to the unprocessed AFBC and PFBC residues described in Table 8, we have also included processed FBC residues in the form of solid compacts (processed by the sorbent/ash blending option) to determine their environmental impact. The processing of FBC residue to minimize leachability by reducing the solid/water contacting surface is discussed in Section 8 of this report.

Table 6

DISTRIBUTION OF SPENT SORBENT/COAL ASH IN FBC BED AND CARRY-OVER

Residue Source	wt % Spent Sorbent	wt % Coal Ash
Bed Material	60-90	10-40
Carry-over (from primary particulate control device, e.g., cyclone)	20-50	50-80
Carry-over, (from final particulate control device, e.g., 3rd-cyclone or fabric filter)	10-40	60-90

Table 7

SUMMARY OF COMPOSITION OF SPENT SORBENT FROM FBC SYSTEMS

Process	Composition (Ca-based molar fraction)			
	$CaSO_4$	CaO	$CaCO_3$	CaS
AFBC, Once-through	0.10-0.50	0.50-0.90	0-0.10	<0.01
PFBC, Once-through	0.10-0.70	0-0.30	0.10-0.80	<0.01
PFBC, Regenerative	0.10-0.40	0.60-0.90	0-0.10	<0.01
PFBC, Adiabatic	0.40-0.70	0-0.30	0-0.30	<0.01

RESIDUES TESTED FOR ENVIRONMENTAL IMPACT

Without Processing

To assess the environmental impact of FBC solid waste disposal, characterization, leaching, and activity tests were performed on carry-over and spent bed materials obtained from experimental FBC units operated by Argonne National Laboratories (ANL),[20] Exxon,[21] Pope, Evans and Robbins (PER),[22] Morgantown Energy Research Center (MERC),[23] Babock and Wilcox, Inc. (B&W),[24] Battelle - Columbus Laboratories,[25] and Combustion Power Company,[26] all of which are conducting FBC development studies under the Department of Energy (DOE), EPA, or the Electric Power Research Institute (EPRI). The FBC residues investigated during this work include spent bed material and carry-over from both the pressurized and atmospheric units operating with either once-through injection of sorbent or with sorbent regeneration.

Table 8 summarizes the samples studied under this contract and the FBC process conditions under which these samples were produced. For the purpose of clarification, spent bed material is sometimes referred to as spent sorbent because the bed material consists predominantly of partially utilized sorbent. The carry-over material is often referred to as fly ash (or ash) and fines; the former is carry-over collected in the primary particulate removal system (first- and second-stage cyclones), and the latter refers to the fines collected from additional particulate filtering devices, such as bag filters, additional cyclones, or stack-gas sampling devices.

After Processing

As part of the effort to identify and evaluate processing methods for reducing the environmental impact of FBC residues, we subjected selected residues to leach testing after processing them into 5-cm cubes. The residues are listed in Table 8 and the specimens tested are in Table 9. The latter were all made from Exxon Run 27 spent bed material and carry-over. Other materials used for comparison tests were natural gypsum and unprocessed residues from Exxon Run 19.6.

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Table 8

PROCESS CONDITIONS OF SAMPLES STUDIED FOR THEIR ENVIRONMENTAL IMPACT ON DISPOSAL

Conditions	PFBC Samples [a]							
	Argonne C2/C3	Argonne VAR-4	Argonne REC-3 [b]	Argonne CCS-10 [c]	Argonne LST-1	Argonne LST-2	Argonne LST-3	Argonne LST-4
Coal	Arkwright	Arkwright	Arkwright	Triangle	Arkwright	Arkwright	Arkwright	Arkwright
Sorbent	Tymochtee dolomite	Tymochtee dolomite	Tymochtee dolomite	Tymochtee dolomite	Limestone 2203	Dolomite 1337	Dolomite 1351	Limestone 1336
Run Length, hr	23	11	80.6	2.6	34.7	25.5	18.4	17.5
Pressure, kPa	810	810	810	152	810	810	810	810
Avg Bed Temp., °C	900-955	900	900	1100	870	870	870	870
Lower Bed Temp., °C	–[d]	–	–	–	–	–	–	–
Gas Velocity, m/s	1.61-1.67	0.7	0.7	1.24	0.76	0.76	0.76	0.76
Expanded Bed Height, m	–	0.91	0.91	0.46	0.91	0.91	0.91	0.91
Settled Bed Height, m	–	–	–	–	–	–	–	–
Coal Feed Rate, kg/h	–	7.9	13.5	–	12.1	11.7	11.7	11.6
Sorbent Feed Rate, kg/h	–	2.6	2.9	–	1.7	3.6	3.1	1.5
Ca/S Molar Ratio	1.1-1.5	1.9	1.5	–	1.5	1.8	1.4	1.4
Excess Air	–	17	17	Reducing	17	17	17	17
SO_2 Emission, ppm	80-375	122	450	67,000	900	160	270	990
NO_x, ppm	135	185	120	–	150	135	185	95
CO, ppm	–	50	64	–	74	50	30	35
CO_2, %	–	18	16	–	16	15	16	17
O_2, %	3.0	3.0	3.2	–	3.5	3.1	2.9	3.0
S Retention, %	82-96	95	79	~65% Regeneration	63	93	89	58
Lb SO_2/M Btu	–	0.23	0.85	–	1.5	0.28	0.47	1.7
Lb NO_2/M Btu	–	0.25	0.16	–	0.18	0.17	0.23	0.12

[a] Identification of experimental FBC units: see text.

[b] Third combustion experiment in ten-cycle combustion/regeneration series of experiments.

[c] Tenth regeneration experiment in ten-cycle combustion/regeneration series of experiments.

[d] Dash indicates data unavailable.

Table 8 (Continued)

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Conditions	PFBC Samples[a]								
	Exxon 8.4	Exxon 19.6	Exxon 26	Exxon 27	Exxon 30.2	Exxon 30.4 (via RS)[a]	Exxon 34	Exxon 43.2	Exxon 43.3
Coal	Arkwright	Champion	Champion	Champion	Champion	Champion	Champion	Illinois No. 6	Illinois No. 6
Sorbent	Grove limestone 1359	Grove limestone 1359	Grove limestone 1359	Pfizer dolomite 1337	Grove limestone 1359	Grove Limestone	Pfizer dolomite 1337	Pfizer 1337 Dolomite	Pfizer 1337 Dolomite
Run Length, hr	11	7.5	15.5	240	8.5	6	13.25	7	6
Pressure, kPa	906-907	930	930	930	920	920	932	870	885
Avg Bed Temp., °C	–[c]	880-888	885-927	829-930	929	835	900	845	940
Lower Bed Temp., °C	877-908	–	949	840-960	945	833	868	850	950
Gas Velocity, m/s	1.77-1.83	2.01-2.04	1.9-2.1	1.7-2.2	2.5	1.9	1.5	1.7	1.77
Expanded Bed Height, m	–	–	–	3-7	–	–	–	5.7	3.13
Settled Bed Height, m	0.66-1.19	1.58	1.12-2.28	–	–	2.26	2.29	2.1	1.9
Coal Feed Rate, kg/h	75-112	113-163	130	112-149	137	120	90	79	93
Sorbent Feed Rate, kg/h	10.3-15.2	–	–	–	–	–	–	–	–
Ca/S Molar Ratio	1.67	2.5	3.7	0-2.5	3.7	3.7	0.75	0.75	0.75
Excess Air	18-72	15	9.5-11.5	8-23	17.2	16.1	20.9	42	25.2
SO_2 Emission, ppm	–	500	140-300	20-1290	137	894	100-300	720	870
NO_x, ppm	50-200	104	180-185	70-210	–	70	52	120	90
CO, ppm	–	–	50	30-110	45	67	61	250	240
CO_2, %	–	11.7-12.3	13	1.1-17	15.1	14.4	15.5	14.0	12.3
O_2, %	–	2.5-3.0	1.8-2.15	1.5-3.9	3.1	2.8	3.5	6.1	4.2
S Retention, %	62	68	81-91	41-100	89	–	–	–	63.1
Lb SO_2/M Btu	1.8	1.0	0.29-0.59	0.03-2.5	–	–	–	–	2.39
Lb NO_2/M Btu	–	0.14	0.25-0.28	0.12-0.30	–	–	–	–	0.178

[a] Identification of experimental FBC units: see text.

[b] Sample obtained from Ralph Stone and Co.[27]

[c] Dash indicates data unavailable.

Table 8 (Continued)

Dwg. 2626C09

Conditions	PFBC Samples [a]					AFBC Samples [a]				
	Exxon 43.5 (via RS)[a]	Exxon 45 Combustor	Exxon 45 Regenerator	Exxon 67	Comb. Power P-403	B & W No. 19	Battelle (Erosion/Corr. Run)	MERC (3/9/77)	PER	PER Shakedown (via RS)[b]
Coal	Illinois No. 6	Champion	–[c]	Illinois No. 6	Illinois No. 6	Pittsburgh No. 8	Illinois. No. 6	Arkwright	Sewickley	Sewickley
Sorbent	Pfizer 1337 Dolomite	Grove Limestone 1359	–	Pfizer 1337 Dolomite	Kaiser Dolomite	Lowellville #4 Limestone (Carbon Limestone Co.)	Grove Limestone	Greer Limestone	Grove Limestone	Greer Limestone
Run Length, hr	4	120	100	100	175	25	1500	~100	–	6
Pressure, kPa	940	780	770	930	405	98.2	101	101	101.3	101
Avg Bed Temp., °C	945	630-900	1010	875-915	855	843	877	838	816	982
Lower Bed Temp., °C	–	705-890	–	–	–	843	–	838	–	–
Gas Velocity, m/s	–	1.19-1.40	0.61	3.23	–	2.13	2.3	1.13	2.7-4.6	–
Expanded Bed Height, m	–	2.92-3.59	2.3	–	–	–	–	0.66	–	–
Settled Bed Height, m	2.18	–	–	–	–	0.38	1.23	0.40	0.3-0.9	0.61
Coal Feed rate, kg/hr	95	79-85	–	122	–	227	69	11.9	272-363	191
Sorbent Feed Rate kg/hr	–	0-6.4	Solid recirculation rate = 45	–	–	77	20.5	(premixed) 4.4	0-182	–
Ca/S Molar Ratio	0.5	0-1.3 Avg = 0.55	–	1.25	–	3	1.8	3.5	–	3
Excess Air, %	25	27.4-39.5	–	19.5	–	–	–	–	–	23
SO_2 Emission, ppm	1330	107-635	Avg = 0.53 m%	640	–	839	520	30 ± 20	–	2000
NO_x, ppm	75	–	–	84	50.2	285	–	400	–	350
CO, ppm	200	–	–	243	–	1000	–	~300	–	700
CO_2, %	14	–	–	13.25	6.2	14.1	–	~10	–	13
O_2, %	4	4.4-5.8	–	3.25	–	2.7	6.8	~8	3	4.5
S Retention, %	–	77	–	–	–	–	~75	–	–	–
Lb SO_2/M Btu	–	–	–	–	–	–	0.9	–	–	–
Lb NO_2/M Btu	–	–	–	–	–	–	–	–	–	–

[a] Identification of experimental FBC units: see text.

[b] Sample obtained from Ralph Stone and Co.[27]

[c] A dash indicates data unavailable.

Table 9

Dwg. 2612C19

PROCESSED FBC SPECIMENS

Sample	Description	Leaching Method
I 1C	Wt ratio fly ash/total solid = 0.358 Wt ratio H_2O/total solid = 0.445 Air cured 7 days	1242-hr continuous shake, wt ratio solid/water = 1/10
I 1D	Same as I 1C	15 × 72-hr intermittent shake, wt ratio solid/water = 1/3
I 2C	Wt ratio fly ash/total solid = 0.358 Wt ratio H_2O/total solid = 0.445 Air cured 11 days	1080-hr continuous shake, wt ratio solid/water = 1/10
I 2D	Same as I 1C	15× 72-hr intermittent shake, wt ratio solid/water = 1/3
I 3C	Wt ratio fly ash/total solid = 0.358 Wt ratio H_2O/total solid = 0.445 Air cured 28 days	1080-hr continuous shake, wt ratio solid/water = 1/10
I 3D	Same as I 3C	15 × 72-hr intermittent shake, wt ratio solid/water = 1/3
I 4C'	Wt ratio fly ash/total solid = 0.100 Wt ratio H_2O/total solid = 0.445 Air cured 60 days	15 × 72-hr intermittent shake compact crushed to powder, wt ratio solid/water = 1/3
I 4D'	Same as I 4C'	15 × 72 hr intermittent shake, original cube (uncrushed), wt ratio solid/water = 1/3
II 1C	Wt ratio fly ash/total solid = 0.100 Wt ratio H_2O/total solid = 0.300 Air cured 7 days	1224-hr continuous shake, wt ratio solid/water = 1/10
II 1D	Same as II 1D	15 × 72-hr intermittent shake, wt ratio solid/water = 1/3
II 3C	Wt ratio fly ash/total solid = 0.100 Wt ratio H_2O/total solid = 0.300 Air cured 28 days	1080-hr continuous shake, wt ratio solid/water = 1/10
II 3D	Same as II 3C	15 × 72-hr intermittent shake wt ratio solid/water = 1/3
II 3E	Wt ratio fly ash/total solid = 0.100 Wt ratio water/total solid = 0.445 Air cured 28 days	1080-hr continuous shake, wt ratio solid/water = 1/10
II 3F	Same as II 3E	15 × 72-hr intermittent shake wt ratio solid/water = 1/3
II 4C	Wt ratio fly ash/total solid = 0.100 Wt ratio water/total solid = 0.300 Air cured 60 days	1080-hr continuous shake, wt ratio solid/water = 1/10
II 4D	Same as II 4C	15 × 72-hr intermittent shake wt ratio solid/water = 1/3
II 4C'	Same as II 4C	15 × 72-hr intermittent shake. compact crushed to powder. wt ratio solid/water = 1/3
II 4D'	Same as II 4C	15 × 72 hr intermittent shake original cube (uncrushed), wt ratio solid/water = 1/3
III 2C	Wt ratio fly ash/total solid = 0.15 Wt ratio H_2O/total solid = 0.3 Air cured 21 days	1080-hr continuous shake, wt ratio solid/water = 1/10
III 2D	Same as III 2C	15 × 72-hr intermittent shake wt ratio solid/water = 1/3
Exxon 19.6 Bed Material	Unprocessed (Spent limestone)	15 × 27-hr intermittent shake wt ratio solid/water = 1/3
Exxon 19.6 Fly Ash	Unprocessed	Same as above
Exxon 27 Sorbent/Ash Mixture	Wt ratio Bed/ash = 80/20, Unprocessed mixture	Same as above
Gypsum	Natural	Same as above

6. EXPERIMENTAL TEST PROGRAM: ENVIRONMENTAL IMPACT

EXPERIMENTAL METHODS

The environmental impact of any material disposed of is a function of its physical and chemical properties as well as of the quantity involved. Potential water pollution problems can be predicted from the chemical characteristics of leachates, such as pH, specific ion concentrations, trace element dissolution, and total dissolved solids (TDS). Disposal of the solid wastes from the fluidized-bed coal combustion process may also create air pollution, odor nuisance, and heat-release problems. To assess the environmental impact of FBC solid waste disposal and the suitability of waste material as landfill, we investigated the physical and chemical characteristics of the residue and its leaching and heat-release properties.

Characterization

Chemical, physical, and morphological characterization of the spent bed and carry-over material was carried out. The methods employed included optical microscopy, scanning electron microscopy (SEM), energy dispersive analysis by X-ray (EDAX), electron microprobe analysis (EMA), X-ray diffraction, thermogravimetric analysis (TGA), emission and atomic absorption spectroscopy, and wet chemical methods.

Leaching Tests

At the time that this study was conducted, no standard EPA leaching test existed for assessing the potential environmental contamination from a solid waste. Since the time that these tests were conducted, an extraction procedure (EP) has been proposed by EPA under Sec. 3001 of RCRA (Federal Register, December 18, 1978)[9] for determining whether a residue is hazardous because of toxicity. The proposed EP specifies that the residue sample be agitated in a container of buffered acetic acid solution for 24 hours, with up to 4 ml of 0.5N acetic acid per gram of solid added during the shaking period in an effort to maintain the pH at 4.9 to 5.2. The residue would be considered toxic if any trace metal element exceeded 10 times the NIPDWR. Westinghouse will conduct some tests in the future that employ EP under their continuing contract with EPA.

Parallel to the EPA effort to develop the EP, ASTM committee 19.12 (subcommittee 19.1203) is also developing a standard leaching test for solid waste materials. It proposes a 48-hour shake method using either type IV reagent water (ASTM D-1193) or pH = 4.5 sodium (Na) acetate-acetic acid buffer.[28]

In the study covered in this report, leachates were induced by the shake test developed by Westinghouse except where otherwise specified. Samples of waste stones were mixed with deionized water in Erlenmeyer flasks at room temperature. An automatic shaker at 70 excursions per minute was used to agitate the mixtures. Among the parameters investigated were sorbent/water loading, sample mixing time, and pH of the leaching medium. The supernatants resulting from this operation were filtered, and the filtrate was determined for pH, specific conductance, TDS, calcium, magnesium, sulfide, sulfate (SO_4), trace metal ion and anion concentrations, and TOC. The solid samples before and after the leaching operation were also analyzed for their chemical and physical characteristics. Since $CaSO_4$ is a major constituent of the waste stone from the fluidized-bed combustion process and leachates contained high calcuim and sulfate concentrations, a naturally occurring gypsum was tested under similar leaching conditions for comparison.

Two shake procedures have been employed. These are described below.

- Continuous shake test. It establishes equilibrium conditions between the solid and its aqueous surrounding and provides the worst possible case with respect to contamination release. Westinghouse has used this method since 1975 as one of the screening tests for determining leaching properties of FBC spent solids. Typically, a 1:10 solid-to-water ratio is used, and the mixture is shaken for up to 400 hours.

- Intermittent shake test. A series of ten to fifteen cycles of a 72-hour shake test was adopted as part of the leachability study to provide leaching rate as a function of time over a long period under worst case conditions. Leachates are analyzed at the end of each interval, and a fresh charge of deionized water is added for each 72-hour leach cycle. Typically, a 1:3 solid-to-water ratio is used.

Both shake tests are severer than conditions anticipated under actual land disposal; results from the shake tests are expected to project the worst case.

Activity Tests

No standard EPA activity test exists that can be applied to FBC residues. Under Sec. 3001 of RCRA, EPA's Office of Solid Waste has proposed some general tests to determine whether a waste is hazardous because of reactivity. These tests concentrate on hazardous properties such as explosiveness and chemical and mechanical instability, however, and do not apply to residual lime.[7,29]

The activity of residual lime in spent FBC materials can be determined by its heat release property on contact with water, as the hydration reaction of CaO is extremely exothermic.[30] Literature on lime reactivity and slaking rate has been reviewed, including the ASTM C110[31] for slaking rate of quick lime (CaO), Murray's study of lime reactivity as a function of porosity and shrinkage characteristics during calcination,[32] and American Water Works' standard on lime for water treatment.

The heat release activity of FBC residue was measured calorimetrically in this study. The temperature rise of a solid/water system containing free CaO is a function of solid/water ratio. In our experimental effort to establish a screening test for the residual activity in spent FBC solids produced under varying processing conditions, a solid/water proportion of 3 g to 20 ml (which is in the bulk range specified by the ASTM-C110 test and by Murray's work) was found empirically to provide much better repeatability than that from a higher solid/water ratio that would give greater magnitude of temperature rise but would lack reproducibility, probably because of local heating. Higher solid/water ratios were also used, however, because they provide higher sensitivity and simulate rainfall onto the disposed solid.

Chromel-alumel thermocouples were used to monitor the temperature rise in the stone/water system with an Omega cold junction compensator and a millivolt recorder. The heat release tests were conducted on the actual spent sorbent and on carry-over fines from the fluidized-bed combustion units. Calcined and uncalcined limestone and dolomite samples were also tested for comparison.

TEST RESULTS

AFBC Residue Characterization and Leachate

Since we anticipate that the first generation of the commercial fluidized-bed combustion process will be a once-through, atmospheric system, we obtained several batches of spent AFBC bed and carry-over materials for testing.

Babcock and Wilcox Residues[24]

Under contract to EPRI, B&W has been operating a 3 ft by 3 ft AFBC unit in Alliance, Ohio. Both the spent-bed and carry-over solids from B&W run 19 were tested for the environmental impact of disposal.

X-ray diffraction which was used to identify the crystalline phases in the solids showed that B&W 19 bed material consists of major quantities of CaO and minor quantities of $CaSO_4$. The carry-over consists of CaO and silicon dioxide (SiO_2) as major, $CaSO_4$ and hematite (αFe_2O_3) as minor, and calcite ($CaCO_3$) and magnetite (Fe_3O_4) as trace species. These results (at best semiquantitative) agree well with the AFBC composition ranges (obtained by wet chemical analysis) shown in Table 5, Section 5.

Results from the leaching tests are summarized in Table 10 for those chemical characteristics resulting from the leaching of the major species - sulfated and nonsulfated calcined limestone. Lower initial values and greater improvement of $CaSO_4$, pH, and specific conductance from the carry-over leachate, in comparison with the spent bed leachate, can be noted here, as would be expected.

The specific conductance is generally a good index for leachate quality because the specific conductance of a leachate provides an approximation of total dissolved solids (TDS). We must emphasize here, however, that the correlation between specific conductance and TDS is not absolute and depends on many factors, such as the molecular weight, the valence, and the mobility of the dissolved species. As an approximation, a specific conductance of 1.5 millimho/cm is generally accepted as equivalent to 1000 mg/ℓ of TDS.[33] Figure 1 plots leachate specific conductance as a function of total leachate volume and time. The difference between bed and carry-over leachate is clear. The Drinking Water Standard (DWS), 500 mg/ℓ TDS, approximated as 0.75 millimho/cm, is very much exceeded by the initial leachate of both the bed and carry-over (2 to 9 millimho/cm) and gradually approached and passed by the carry-over leachate after nine 72-hour leach cycles.

Because of the large number of residues to be studied during this investigation, and because the carry-over solid and leachate generally contain higher levels of trace elements (as will be illustrated for MERC residue in a later section), the entire spectrum of solid and leachate characterization was performed only on the carry-over material of B&W run 19 residue. Results presented in Table 11 show that the trace elements meet the DWS and the TOC is below the detectable level, but calcium, sulfate, pH, and TDS exceed the DWS. These results agree well with those reported previously.[5]

Heat release test results indicated higher residual lime activity in the spent bed material than in the carry-over, as would be expected with the higher CaO content in the spent bed. The heat release results will be discussed in detail later under Thermal Activity Tests. Both

Dwg. 1701880

Table 10

LEACHATE CHARACTERISTICS OF B&W 19 RESIDUES

Residue	Chemical Characteristics	Intermittent Shake, no. of 72-hr intervals															Continuous Shake, hr	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	100	200
Bed	pH	12.0	12.2	12.1	12.2	12.2	12.2	12.1	12.2	12.2	12.0	12.2	12.4	12.2	12.0	12.0	12.1	12.2
	Sp. Conductance millimho/cm	8.48	8.72	8.34	8.7	8.22	8.78	8.33	9.00	7.75	8.64	8.69	8.05	7.66	7.04	7.95	9.36	9.24
	Ca, mg/ℓ	1136	1404	1424	1384	1352	1400	1320	1480	1344	1396	1360	1084	1264	1012	996	1364	1392
	SO_4, mg/ℓ	1352	1094	1236	1273	1248	1298	1128	1325	1128	1298	1213	1353	1071	1175	1225	1175	1209
Carry-over	pH	12.2	11.9	11.8	11.7	11.7	11.7	11.5	11.4	10.6	10.7	10.8	10.8	10.5	9.6	9.2	12.0	11.9
	Sp. Conductance millimho/cm	7.65	4.06	2.46	2.32	1.92	1.46	1.26	1.24	0.38	0.64	0.38	0.64	0.38	0.47	0.49	8.1	6.47
	Ca, mg/ℓ	888	88	64	36	84	70	32	32	24	14	40	32	44	80	88	1288	1184
	SO_4, mg/ℓ	1325	122	0	9	11	15	15	25	50	75	88	75	74	175	216	1273	1248

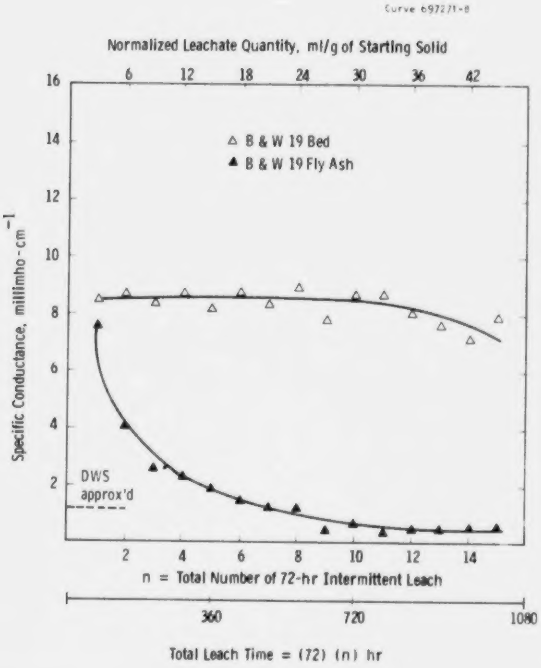


Figure 1 - Leachate Quality as a Function of Intermittent Leaching

the AFBC bed and carry-over materials released more heat than did the PFBC residue tested and reported in the previous report.[5] This too, is as expected, since the PFBC residue would be presumed to have a greater fraction of its calcium content in the form of $CaCO_3$, which unlike CaO, will not hydrate and release heat.

PER Residue[22,27]

Two PER residues produced from a 0.46-by-1.83-m AFBC unit funded by the Department of Energy (DOE) were tested during this reporting period. These were a spent bed material from a shakedown test and a carry-over from a different run (origin not identified). Both residues were obtained through Ralph Stone and Co.[27] They had obtained the material from PER and had also tested it. The shakedown bed residue was identified by X-ray diffraction to contain CaO, SiO_2, calcium hydroxide

Table 11

Dwg. 1709B93

SOLID AND LEACHATE CHARACTERISTICS OF B&W 19 CARRY-OVER
(200-hr Continuous Shake Test)

Substance	Solid, ppm	Leachate, mg/ℓ	DWS,[*] mg/ℓ
Al		< 1	
Ag	< 1	< 0.01	0.05
As		< 0.003	0.05
B	200	0.01	
Ba		< 1	1.0
Be	5	< 0.01	
Bi	30	< 0.01	
Ca	9.44%	▨ 1,184	200
Cd	< 3	< 0.01	0.01
Co	5	< 0.01	
Cr	50	< 0.01	0.05
Cu	30	< 0.05	1.0
Fe		< 0.05	0.3
Hg		< 0.002	0.002
Mg	0.096%	< 10	150
Mn	140	< 0.01	0.05
Mo	10	0.15	
Na	200	3	
Ni	20	< 0.05	2.0
Pb	< 5	< 0.01	0.05
Sb	< 33	< 0.01	
Se		< 0.003	0.01
Si		1	
Sn	< 10	< 0.01	1.0
Sr	200	> 10	
Ti	> 1,000	< 0.05	
V	40	< 0.01	
Zn	< 33	< 1	5.0
Zr		< 1	
SO_4	3.36%	▨ 1,247.5	250
$S^=$	0.094%	< 10	
F		< 1	2.4
Cl		12	250
NO_3 (as N)		< 10	10
TOC		< 10	
pH		▨ 11.9	6.5 to 9.2
SC, µmho/cm		▨ 6,470	~750

[*] DWS – NIPDWR, USPHS, and WHO drinking water standards.

▨ exceeds DWS.

($Ca(OH)_2$), α-Fe_2O_3, and $CaSO_4$ in decreasing concentrations. The trace quantity of $CaSO_4$ is not typical of spent bed material; one would expect bed material to contain about 25 molar percent of $CaSO_4$ (Table 5). The PER carry-over material consists of major quantities of CaO and SiO_2, minor quantities of $CaSO_4$ and α-Fe_2O_3, and trace amounts $CaCO_3$ and Fe_3O_4. Chemical analysis data (shown on Table 12 along with leachate characteristics that will be discussed later) confirmed these findings.

Figure 2 shows SEM photomicrographs and EDAX spectra of the PER bed and carry-over. One can see the low sulfur concentration in the EDAX spectrum of the PER shakedown bed material also. SEM and EDAX of the carry-over show the material to have chemical characteristics one would expect to find in bed material rather than in carry-over. We believed that the material was collected from the primary cyclone without recycle and is, therefore, very much like the bed material, although the actual identity of the run was not known.

Tables 12 and 13 summarize the concentrations of major and trace species in solids and leachates from the shake tests. Calcium ion fluctuation in the leachate was caused by the ready formation of a white precipitate during filtration and handling of the leachate in air. This white precipitate was identified by X-ray diffraction and TG to be $CaCO_3$. Figure 3 shows a SEM and EDAX spectrum of the white crystalline agreeing with the X-ray and TG results. Since the PER shakedown test bed material consists mostly of CaO, its leachate forms carbonation products most readily; other residues, with more typical (lower) CaO contents (and higher $CaSO_4$ contents) did not show this tendency to form precipitates. Due to the very low $CaSO_4$ concentration in the PER shakedown bed material, its leachate displayed much lower sulfate characteristics than would the residue of a typical FBC system. Table 13 shows that TOC and trace metal elements are sufficiently low in the PER leachate to meet the existing DWS. Heat-release property will be reported in a later section.

Table 12 Dwg. 1709891

SOLID AND LEACHATE CHARACTERISTICS OF PER RESIDUES
(200-Hr Continuous Shake Test)

Substance	PER Solids, wt%[a]		PER Leachates, mg/ℓ[a]		DWS,[b] mg/ℓ
	(1)	(2)	(1)	(2)	
Al	> 10	> 10	0.05	1.0	
Ag			< 0.01	< 0.01	0.05
As	0.003	0.003	< 0.002	< 0.002	0.05
B	0.01	0.01	< 0.05	0.8	
Ba			< 1	≤ 1.0	1.0
Be	0.0002	0.0001	< 0.01	< 0.01	
Bi	< 0.0003	< 0.0003	< 0.01	< 0.01	
Ca	27.52	16.64	720	1,264	200
Cd	< 0.003	< 0.003	< 0.01	< 0.01	0.01
Co	< 0.0005	< 0.0005	< 0.05	< 0.05	
Cr	0.003	0.003	< 0.05	< 0.05	0.05
Cu	0.005	0.005	< 0.05	< 0.05	1.0
Fe	> 10	> 10	< 0.1	< 0.1	0.3
Hg			< 0.001	< 0.001	0.002
Mg	3.93	2.88	14.4	14.4	150
Mn	0.02	0.01	< 0.05	< 0.05	0.05
Mo	0.002	0.001	0.05	0.2	
Na	0.1	0.1	> 5	> 5	
Ni	0.005	0.005	< 0.05	< 0.05	2.0
Pb	0.001	0.001	< 0.05	< 0.05	0.05
Sb			< 0.05	< 0.05	
Se			< 0.003	< 0.003	0.01
Si	> 10	> 10	2	> 5	
Sn	< 0.003	< 0.003	< 0.05	< 0.05	1.0
Sr			> 5	> 5	
Ti	0.1	0.1	< 0.05	< 0.05	
V	0.001	0.001	< 0.05	< 0.05	
Zn	0.007	0.01	< 1	< 1	5.0
Zr	0.01	0.01	< 0.1	< 0.1	
SO_4	26.4	45.76	< 10	1,410	250
TOC			< 10	< 10	
pH			12.0	12.1	6.5 to 9.2
SC, µmho/cm			7,850	8,060	~750

[a] (1) PER shakedown bed

(2) PER carry-over

[b] DWS - NIPDWR, USPHS, and WHO drinking water standards.

▨ exceeds DWS

Dwg. 1701881

Table 13

LEACHATE CHARACTERISTICS OF PER RESIDUES

Residue	Chemical Characteristics	Intermittent Shake, no. of 72-hr intervals															Continuous Shake, hr	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	100	200
Bed	pH	12.0	12.3	12.1	12.1	11.9	12.2	12.2	12.1	12.1	11.9	11.9	12.1	11.9	11.5	11 6	12.2	12.0
	Sp. Conductance millimho/cm	7.55	7.37	7.22	7.03	6.98	6.98	6.69	6.84	6.77	7.08	7.15	6.9	6.8	7.32	6.79	7.96	7.85
	Ca, mg/ℓ	-	400	400	608	-	472	-	-	528	496	600	588	500	504	496	244	720
	SO_4, mg/ℓ	298	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	< 10	100	< 10
Carry-over	pH	12.2	12.4	12.2	12.2	12.1	12.3	12.2	12.2	12.2	12.1	12.1	12.2	12.0	12.0	12.0	12.1	12.1
	Sp. Conductance millimho/cm	7.78	7.55	7.39	7.49	7.48	7.35	7.35	7.3	7.02	6.72	6.46	5.45	5.68	3.7	3.15	8.52	8.06
	Ca, mg/ℓ	976	960	952	1136	904	944	936	900	1008	856	876	704	736	448	424	1056	1264
	SO_4, mg/ℓ	1298	1338	1260	1138	1082	1260	1353	1128	1128	1150	850	704	778	778	590	1623	1410

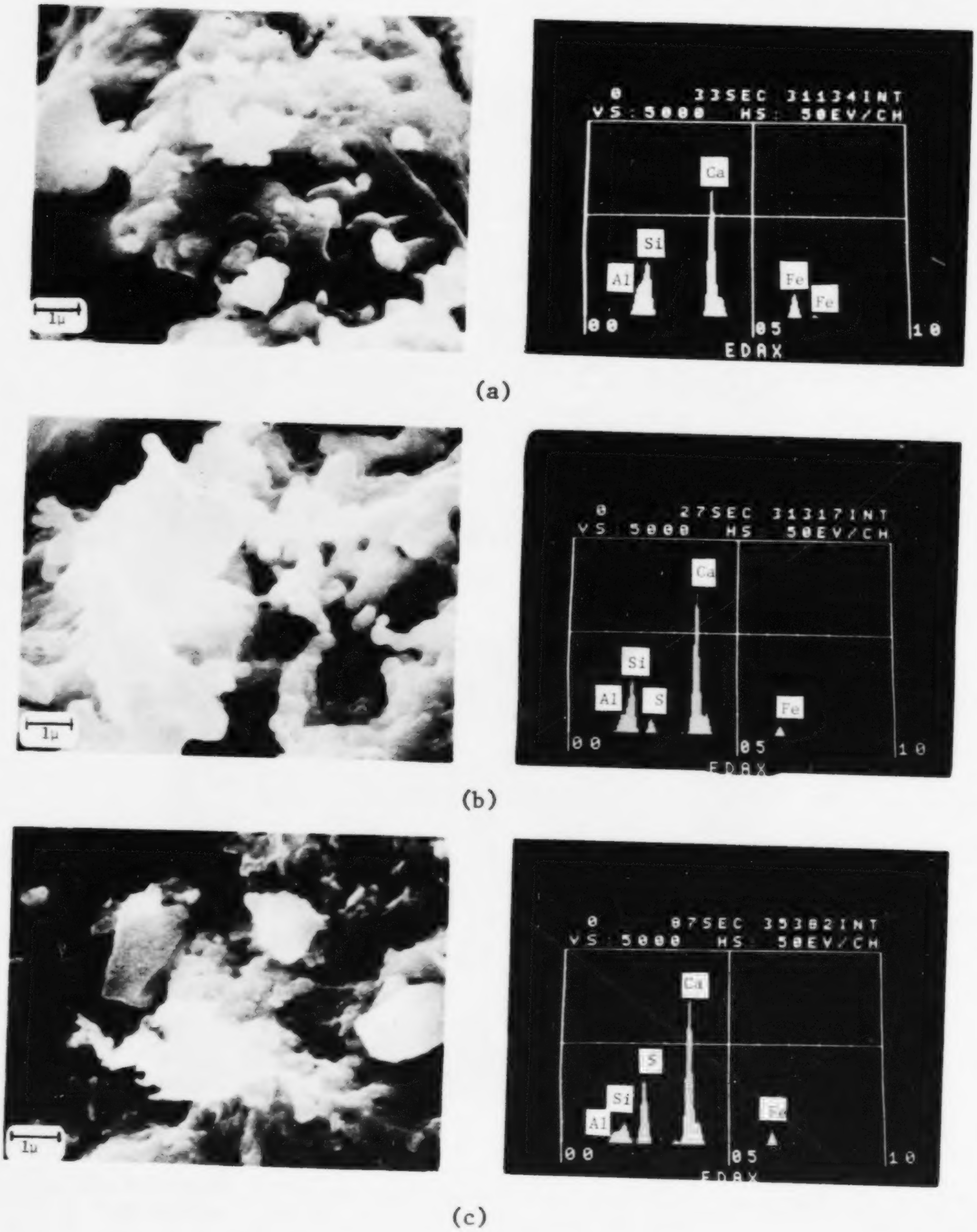
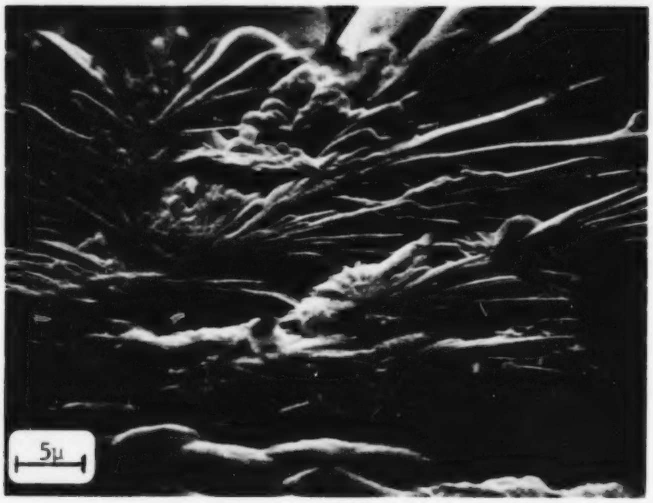
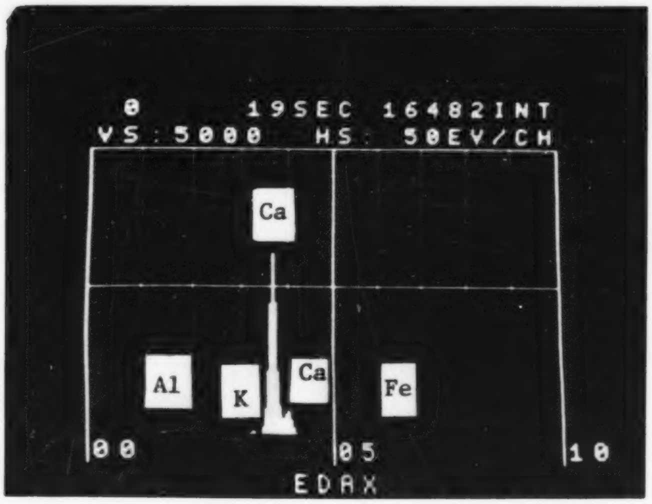


Figure 2 - SEM and EDAX of (a) RS-PER Shakedown Bed Material, Particle Surface, (b) RS-PER Shakedown Bed, Fractured Surface, (c) RS-PER Carry-over



(a)



(b)

Figure 3 - SEM Photomicrograph (a) and EDAX Spectrum (b) of the White Precipitate Formed Readily in Air from the Leachate from PER Bed Material and Carry-over

Since the PER residues used in this study were of uncertain or nontypical origin, we recommend further investigation when more representative samples are available.

Battelle Residue[25]

In August and November of 1977, we obtained from the Battelle Columbus Laboratories two batches of bed and carry-over (cyclone) materials withdrawn during a corrosion/erosion run (600 to 1000 hr into the test) and at the end of the 1500-hr continuous run. The Battelle corrosion/erosion experiment was conducted in a 24-in. diameter AFBC unit at 877°C, using Illinois No. 6 coal and Grove limestone with a calcium-to-sulfur ratio of Ca/S = 1.8. The objective of the DOE-funded run was to conduct corrosion/erosion experiments on candidate heat-exchanger and superheater tube materials exposed to high-temperature (e.g., 593 to 870°C) gaseous corrosion and particulate erosion in the bed of an atmospheric fluidized-bed coal combustor containing limestone as a sulfur oxide (SO_x) sorbent, to establish engineering durability data as a function of materials properties.

Chemical analyses summarized in Table 14 showed similar compositions for the two batches of samples withdrawn at different times into the same run (one at 600 to 1000 hr into the test and one at the end of the 1500-hr run). Because of their similaritv, only the solids withdrawn at the end of the 1500-hr run were used in the leaching studies.

Table 15 summarizes the chemical characteristics of the 200-hr leachates from the Battelle bed and carry-over materials. As we expected, both leachates had much higher calcium, SO_4, pH, and specific conductance than do the DWS, because of the dissolution of the major species, CaO and $CaSO_4$, but did not exceed any of the trace elements where DWS existed. Figure 4 presents the results from the intermittent leaching tests. The difference between the bed and carry-over leachates is clearly demonstrated by the much more rapid improvement in the leachate quality of the latter. Results from the Battelle residues testing, in general, agree well with those previously reported.

Table 14

Dwg. 7709A92

CHEMICAL ANALYSIS OF BATTELLE FBC RESIDUES
FROM THE 1500-HR CORROSION/EROSION TEST

Sample	Wet Chemical Method						X-Ray Diffraction				
	Ca	Mg	$S^{=}$	SO_4	$CaSO_4$*	CaO*	$CaSO_4$	CaO	$Ca(OH)_2$	SiO_2	αFe_2O_3
Bed, 1500 hr	33.8	1.0	0.05	39.2	55.5	24.4	Major	Minor	Lo-minor	Lo-minor	–
Bed, 1000 hr	30.8	0.14	0.02	35.6	50.4	22.4	Major	Minor	Lo-minor	Lo-minor	–
Carry-over, 1500 hr	27.0	0.91	0.4	25.6	36.3	22.8	Major	Minor	Lo-minor	Major	Lo-minor
Carry-over, 600 hr	25.6	0.14	0.02	27.0	38.2	20.1	Major	Minor	Lo-minor	Major	Lo-minor

*Estimated by chemical analysis data

Table 15

Dwg. 1694B71

CHEMICAL CHARACTERISTICS OF LEACHATES FROM BATTELLE FBC RESIDUES (200-hr Continuous Shake Test)

Substance	Leachate Characteristics, ppm		Drinking Water Standards, ppm
	Bed	Carry-over	
Al	<1	<1	
Ag	<0.01	<0.01	0.05
As	<0.05	<0.05	0.05
B	> 4	2	
Ba	<1	<1	1.0
Be	<0.01	<0.01	
Bi	<0.01	<0.01	
Ca	1384	928	200
Cd	<0.01	<0.01	0.01
Co	<0.05	<0.05	
Cr	0.05	0.04	0.05
Cu	<0.1	<0.1	1.0
Fe	<0.02	<0.02	0.3
Hg	<0.002	<0.002	0.002
Mg	<1	<1	150
Mn	<0.01	<0.01	0.05
Mo	0.26	0.08	
Na	80	7.6	
Ni	<0.05	<0.05	2.0
Pb	<0.01	0.05	0.05
Sb	<0.05	<0.05	
Se	<0.01	<0.01	0.01
Si	<1	<1	
Sn	<0.05	<0.05	1.0
Sr	> 4	5	
Ti	<1	<1	
V	<0.03	<0.03	
Zn	<1	<1	5.0
Zr	<1	<1	
F	<1	<1	2.4
Cl	12	12	250
NO_3 (as N)	<10	<10	10
SO_4	1460	1175	250
TOC	<10	<10	
pH	12.2	12.1	6.5 to 9.2
Sp. Cond. (μ-mho/cm)	9040	8000	~750

a Drinking Water Standards: NIPDWR: USPHS and WHO Drinking Water Standards

▨ Exceed the drinking water standards

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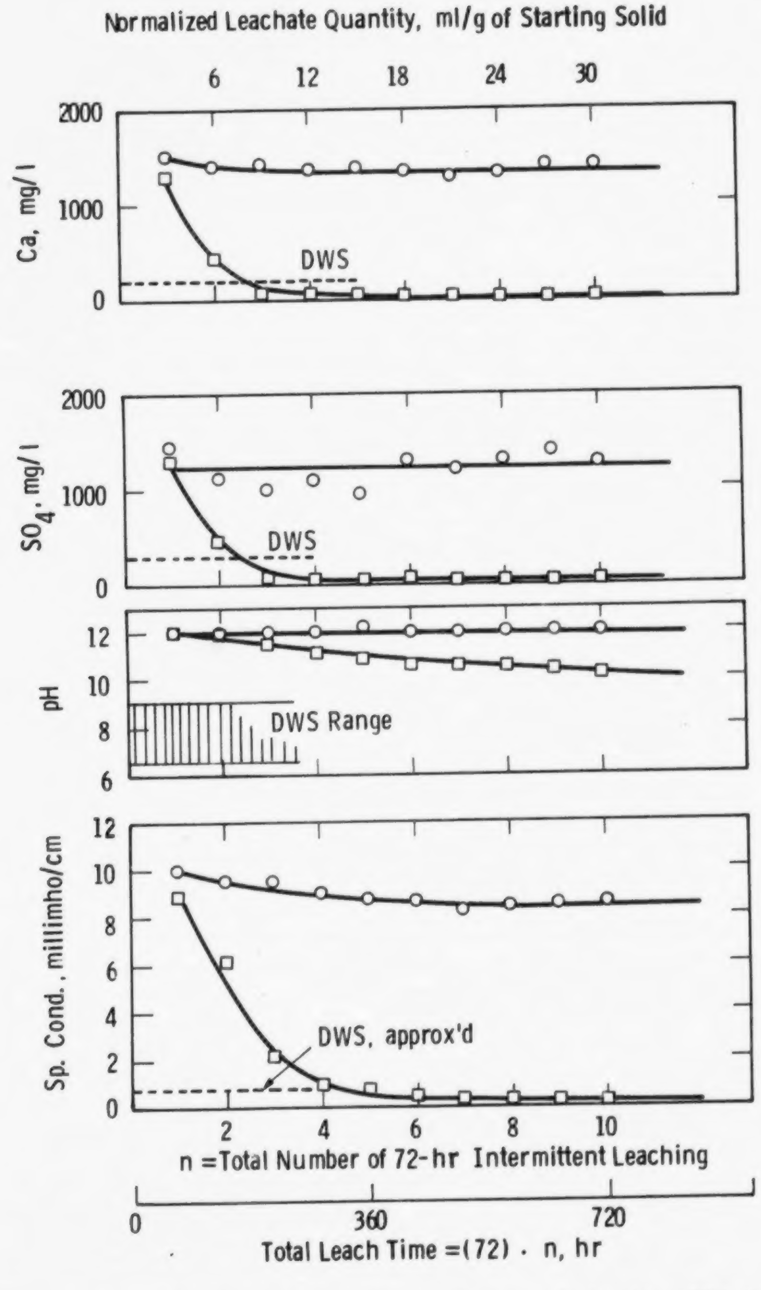

Figure 4 - Leachate Characteristics of Battelle FBC Bed (o) and Carry-over Material (□) as a Function of 72-hr Carry-over Intermittent Leaching

MERC Residue[23]

The MERC residue was produced from a spent sorbent production run requested by Westinghouse as part of EPA's environmental testing program on the MERC 18-in.-id AFBC unit. This combustor includes two cyclones in series on the flue gas (cyclone 1 followed by cyclone 2), followed by two bag filters in parallel. Batches of bed material (three samples), cyclone ash (five samples), and bag-filter fines (two samples) were collected at various times throughout the 100-hr continuous run.

Table 16 summarizes the compounds identified by X-ray diffraction. Because of the nature of the X-ray diffraction method, we shall not attempt to go beyond semiquantitative description of the results, major minor, and trace. All of these materials (bed, cyclone, and bag filter) were high in $CaSO_4$. Of the unsulfated portion, the bed material contained more CaO (or $Ca(OH)_2$ formed by CaO hydration in air), while the fines contained more $CaCO_3$. This explains the lower heat release by ash and fines reported in detail in a later section. When the bed material was separated physically, we found that the white (interior) particles were mostly CaO and $Ca(OH)_2$, the grey particles were unsulfated $CaCO_3$, and the darker particles were rich in SiO_2 and Fe_2O_3. The raw sorbent (Greer limestone) and coal (Arkwright) were also analyzed. The Greer limestone was found to consist of major amounts of $CaCO_3$, minor SiO_2, and dolomite ($CaMg(CO_3)_2$) with trace $CaSO_4$. The crystalline species in the coal were found to be SiO_2 and iron sulfide (FeS).

Table 17 summarizes the leaching results by the continuous shake method of three batches of bed material collected at three different times, two batches of cyclone ash from the two different cyclones and two batches of bag-filter fines from two different filters. Agreeing with the previous leaching results from other FBC spent materials, high pH, TDS, calcium, and SO_4 resulted from the bed material leachate. Material from cyclone 1 produced leachates similar to the bed material; this result is not surprising, since this cyclone is the first of the series of control devices on the unit and, thus, collects the coarsest

Dwg. 1690B61

Table 16

IDENTIFICATION OF SPENT MERC BED MATERIAL AND CARRY-OVER

Sample	Separation	Chemical Composition						Others
		$CaSO_4$	$CaCO_3$ (Calcite)	CaO	$Ca(OH)_2$	SiO_2	Fe_2O_3	
MERC Bed, 3/8	General grind	Major	Trace	Trace	Minor	Trace	—	Possible trace of vaterite $CaCO_3$
"	Brown throughout	Major	—	Trace	Trace	Hi Minor	—	—
"	Thin brown OD white ID	Trace	Trace	Trace	Major	Trace	—	Trace vaterite $CaCO_3$
"	Brown OD black center	Minor	—	—	—	Trace	Major	—
"	Grey throughout	Trace	Major	—	—	Hi Minor	—	—
"	Black	Lo Minor	Trace	—	—	Major	—	—
MERC Bed, 3/9	General grind	Major	Trace	Lo Minor	Trace	Hi Minor	—	—
"	Black	Trace		Trace		Major	—	—
MERC Cyclone 2 Carry-over	General grind	Major	Lo Minor	Lo Minor	—	Major	Minor	—
MERC Bag Filter 1&2 Fines	General grind	Major	Minor	Trace	—	Major	Minor	—
Greer Limestone	General grind	Trace	Major	—	—	Minor	—	Minor $CaMg(CO_3)_2$
Arkwright Coal	General grind	—	—	—	—	Minor	—	Major FeS

Table 17

SUMMARY OF LEACHING RESULTS OF MERC SAMPLES BY CONTINUOUS SHAKE METHOD

Sample	Solid/ Water Ratio	Leaching Time, hr	Leachate Characteristics			
			pH	Specific Conductance, millimho/ cm	mg/l	SO_4, mg/l
MERC Bed, 3/9	1:10	220	12.0	8.93	1336	1273
MERC Bed, 3/9	1:10	400	11.9	7.61	1188	1690
MERC Bed, 3/8	1:10	220	11.9	8.38	1232	1395
MERC Bed, 3/8	1:10	400	11.9	7.80	1208	1370
MERC Bed, 3/8-9	1:10	200	12.0	10.1	1488	1395
MERC Bed, 3/8-9	1:10	400	11.9	8.48	1384	1285
MERC Cyclone 2	1:10	220	11.8	4.78	8	282
MERC Cyclone 2	1:10	400	11.6	2.98	0	374
MERC Cyclone 1	1:10	200	12.0	9.14	1208	1225
MERC Cyclone 1	1:10	400	11.9	8.94	1244	1020
MERC Bag Filter 1&2	1:10	220	10.8	3.44	220	830
MERC Bag Filter 1&2	1:10	400	10.6	2.39	48	488
MERC Bag Filter 2	1:10	200	11.6	3.2	48	276
MERC Bag Filter 2	1:10	400	11.1	2.36	40	514
Greer Limestone	1:10	220	8.0	0.2	16	30
Greer Limestone	1:10	400	8.0	0.2	16	37
Arkwright Coal	1:10	220	2.8	2.02	96	960
Arkwright Coal	1:10	400	2.8	1.83	104	1050

carry-over, which is likely to be most like the bed material. Leachates from cyclone 2 and the bag-filter fines had lower pH, TDS, calcium, and SO_4. In every case leachate quality improved between the 200-hr and 400-hr continuous shake time, most likely because of carbonation of dissolved $Ca(OH)_2$ by dissolved carbon dioxide (CO_2). Leaching results from the raw sorbent and coal are also reported in Table 17. Greer limestone, which was practically insoluble, produced leachate of very good quality, while Arkwright coal produced highly acidic (pH = 2.8) leachate with a high SO_4 concentration.

Figure 5 summarizes the results from intermittent leaching for the MERC materials. Leachate characteristics from two batches of bed material collected at different times in the test were in good agreement in the intermittent leach tests. There was little change over time or with increasing total leachate volume passing through the bed material. Leachates from the cyclone and bag-filter fines showed improvement with total leachate volume and time.

In addition to those using deionized water, continuous shake leaching tests were also conducted using CO_2-saturated deionized water (pH = 4) to simulate the leaching that might take place in the environment due to exposure of the residue to rainwater or surface water. Table 18 summarizes the chemical characteristics, including major and trace metal and anions, and the TOC for leachates induced with deionized water and CO_2-saturated water media. Several points are worth noting, based on the test results summarized in Tables 17 and 18:

- The leachate of MERC bed material appeared to be similar to leachates from all the other FBC residues examined previously.
- Unlike all the previous FBC leachates tested, the leachate from MERC carry-over material exceeded the drinking water standards for two elements -- barium (in one of the four carry-over leachates indicated in Table 18) and chromium (in all four carry-over leachates). Note, also, that the DWS standards are used here for comparative reference only.

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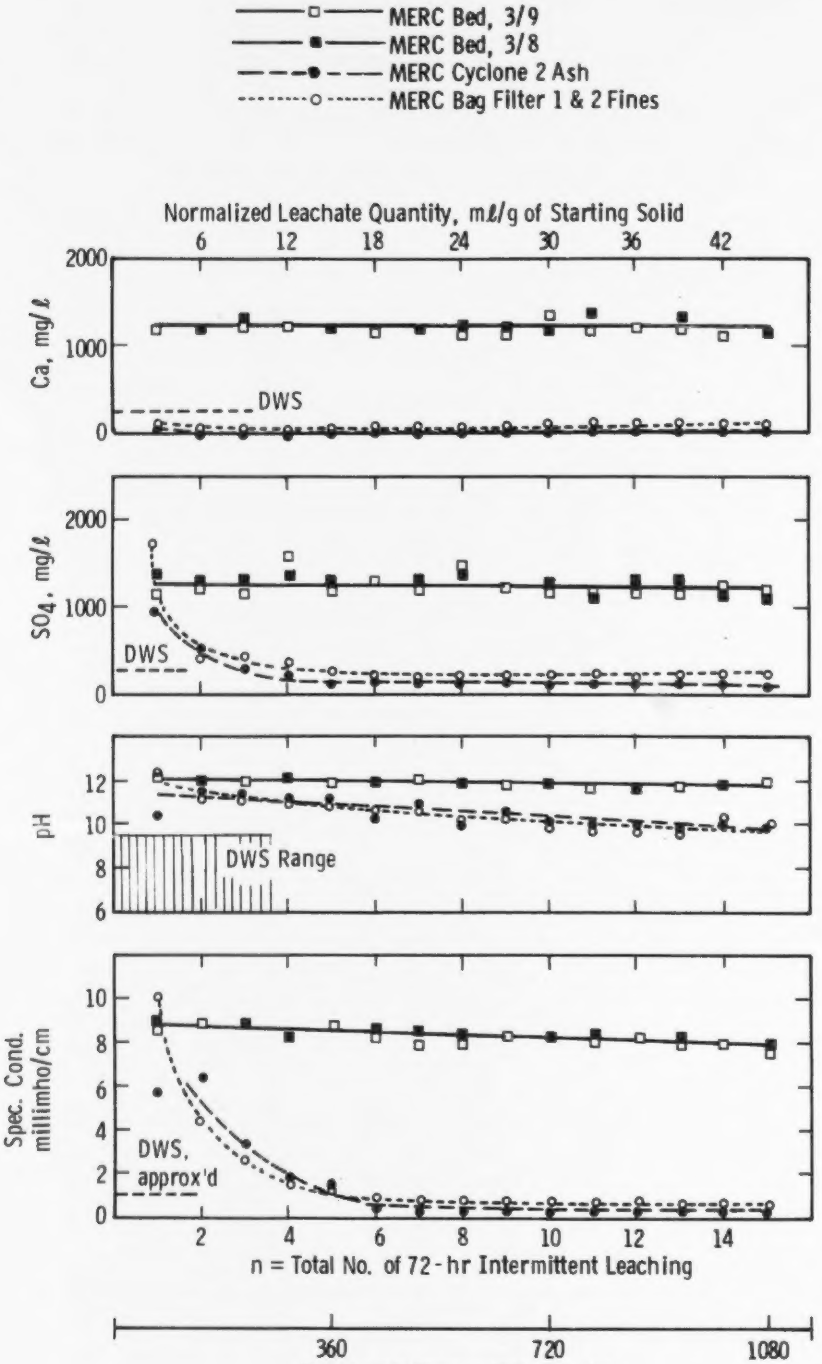

Figure 5 - Leachate Characteristics of Spent MERC Bed Material, Ash, and Fines as a Function of Intermittent Leaching

Table 18

Dwg. 2616C60

SOLID AND LEACHATE CHARACTERISTICS OF MERC-AFBC RESIDUES: EFFECT OF USING CO$_2$-SATURATED WATER AS LEACHING MEDIUM (200-hr Continuous Shake Tests)

Substance	Solid, ppm[a]			Leachate, ppm[b]						Drinking Water Standards[c]
	(1)	(2)	(3)	(1A)	(2A)	(3A)	(1B)	(2B)	(2B)	
Al	Major	Major	Major	<1	2	>2	<1	<1	<0.1	
Ag	<1	<1	<1	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.05
As				<.05	<0.05	<0.05	<0.05	<0.05	<0.05	0.05
B	50	500	500	<.1	<0.2	3	<0.1	<.1	0.1	
Ba				<1	▨ 2	<1	<1	<1	<1	1.0
Be	10	10	10	<0.01	<0.01	<.01	<0.01	<0.01	<0.01	
Bi	<10	<10	<10	<0.01	<0.01	<.01	<0.01	<0.01	<0.01	
Ca	39%	18%	16%	▨ 1276	16	▨ 200	▨ 1336	8	▨ 220	200
Cd	<3	<3	<3	<0.01	<0.01	<.01	<0.01	<0.01	<0.01	0.01
Co	5	15	15	<0.02	<0.02	<.02	<0.02	<0.02	<0.02	
Cr	60	100	100	0.04	▨ 0.3	▨ 1.0	0.04	▨ 0.35	▨ 0.67	0.05
Cu	30	100	100	<0.1	<0.1	<.1	<0.1	<.1	<0.1	1.0
Fe	Major	Major	Major	<0.1	<0.2	<0.2	<0.2	<0.2	<0.2	0.3
Hg				<0.002	<0.002	<0.002	<0.002	<.002	<0.002	0.002
Mg	>1000	>1000	>1000	<1	<1	1	<1	<1	<1	150
Mn	190	220	280	<.01	<0.01	<0.01	<0.01	<.01	<.01	0.05
Mo	30	10	10	0.04	0.4	>2	0.04	0.5	>2	
Na	>1000	>1000	>1000	4	>>4	>>4	9	206	209	
Ni	40	70	70	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	2.0
Pb	<10	100	130	<0.01	<0.01	0.04	<0.01	<0.01	<0.02	0.05
Sb	<33	<33	<33	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	
Se				<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	0.01
Si	Major	Major	Major	<0.2	>2	>2	<0.02	2	>2	
Sn	<10	<10	<10	<0.04	<0.04	<0.04	<0.04	<0.04	<0.04	1.0
Sr	500	1000	1000	4	>4	>>4	4	>>4	>>4	
Ti	>1000	>1000	>1000	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	
V	40	100	80	<0.02	<0.03	0.4	<0.02	0.02	0.5	
Zn	≤33	100	100	<1	<1	<1	<1	<1	<1	5.0
Zr				<1	<1	<1	<1	<1	<1	
Cl				16	17	148	16	120	▨ 335	250
F				<1	<1	<1	<1	<1	2.4	2.4
Br				<1	<1	2.6	<1	2.4	2.9	
NO$_2$				<1	<1	<1	<1	<1	<1	
NO$_3$ (as N)				<1	<1	<1	<1	≤1	3	10
PO$_4$				<1	<1	<1	<1	<1	<1	
SO$_4$	20%	13%	12%	▨ 1350	▨ 370	▨ 830	▨ 1260	▨ 370	▨ 650	250
TOC				<10	<10	<30	<10	<10	<10	
pH				▨ 12.0	▨ 11.8	▨ 10.8	▨ 11.8	▨ 11.7	▨ 10.9	6.5 to 9.2
SC (μ hos/cm)				▨ 8930	▨ 4780	▨ 3440	▨ 8560	▨ 4390	▨ 3210	~750

Note [a] MERC solids: (1), (2), and (3) denote bed, cyclone 2, and bag filter materials respectively

[b] Samples (1A), (2A), and (3A) are deionized water–induced leachates from the MERC bed, cyclone, and bag filter materials Leachates (1B), (2B), and (3B) are generated using CO$_2$ – saturated deionized water from the MERC bed, cyclone, and bag filter materials respectively

[c] Drinking Water Standards: NIPDWR, USPHS, and WHO Drinking Water Standards

▨ Exceed the Drinking Water Standards

- The TOC was also higher in the leachate from MERC bag-filter material ($\leq$30 ppm) than from that found in all the other FBC leachates (<10 ppm).
- The pH and major species (calcium, SO_4, and TDS) decreased with decreasing particle size (in the order of bed, cyclone, and bag-filter materials), in both the solids and their leachates. This observation confirms the expectation that the spent sorbent (the cause of the high pH, calcium, SO_4, and TDS levels) is present primarily in the coarser fractions.
- Trace elements (e.g., B, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sr, V, Zn, Cl, Br) increased with decreasing particle size in the solids and, in many cases, in their leachates as well. That is, trace elements were more concentrated in the carry-over materials and their leachates (bag-filter catch > cyclone 2 > bed material).
- The effect of leaching with CO_2-saturated deionized water was not pronounced, probably because of the high alkaline content in the FBC residues; the mild acidic effect of the CO_2 is quickly neutralized.

Leaching property was also investigated using a sodium acetate-acetic acid buffer solution with pH = 4.5 ± 0.1. Results will be discussed in a later section, together with acid leaching of many other FBC residues.

Earlier results using PFBC residue showed improvement of leachate quality by codisposal of the spent bed material with the carry-over.[5,34] Codisposal of MERC bed, cyclone, and bag-filter residue was also investigated here. A mixture of 60:20:20 of bed:cyclone:bag-filter materials was used in the two repeated leaching tests. This mix ratio was selected as being reasonably representative of the ratio in which the materials would be disposed of in a commercial AFBC facility. The results of the two tests were different. Figure 6 shows these results and compares them with leachate conductance from unmixed bed, cyclone,

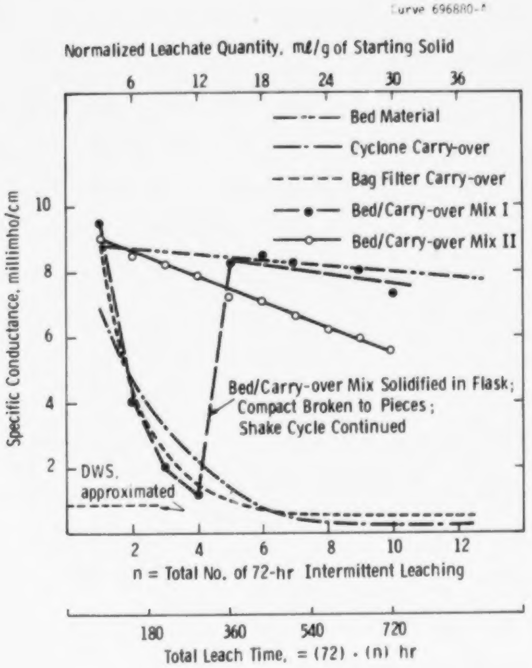

Figure 6 - Leachate Characteristics from Codisposal of MERC Bed and Carry-over Materials

and bag-filter solids. In the first test (MX I), leachate quality improved rapidly as the solid mixture solidified at the bottom of the flask after four 72-hr cycles. The cementlike compact was then broken, and leaching cycles continued. This accounts for the discontinuity of the MX I result on Figure 6. The experiment was repeated in the MX II test, which did not solidify, but its leachate showed slow, steady improvement over total leaching time and leachate volume. These experiments demonstrated:

- The possibility of the residue hardening (cementlike setting) when spent bed and carry-over materials are disposed of together in a landfill
- The effect of the fissuring of the hardened residue on the resultant leachate

- The potential of reduced environmental impact from codisposal of spent bed material with the carry-over due to the pozzolanic reactions.

Acid mine neutralization experiments were also conducted, using mixtures of Arkwright coal and MERC residues. Results showed that spent FBC sorbent can be an efficient neutralization agent for the acid mine drainage because of the high free-lime content. Westinghouse is continuing work in this area under contract to EPA.

PFBC Residue Characterization and Leachate

Exxon Miniplant

Most of the FBC residues investigated and reported previously were from PFBC once-through systems. The PFBC residues tested during this reporting period include spent bed material, cyclone carry-over, and stack fines from the Exxon miniplant at Linden, New Jersey.[21] The miniplant consists of a 32-cm-id pressurized combustor; it also includes a 21.6-cm-id regenerator that can be used to regenerate the spent sorbent for reuse, if desired. We also obtained some regenerator residue samples for testing. Table 19 summarizes the chemical identification by X-ray diffraction of the Exxon residues investigated during this reporting period.

Exxon run 43 is a once-through PFBC run using dolomite operated at different bed temperatures - for example, Exxon 43.2 at 845°C and Exxon 43.3 at 940°C. At the lower temperature, the calcium fraction of the dolomite would not be expected to calcine, so only the magnesium fraction would calcine; at the higher temperature, both fractions should calcine. The mixed spent sorbent, therefore, is expected to contain both the half-calcined material from the lower-temperature portion of the test and the fully calcined dolomite from the higher temperature test. Indeed, X-ray diffraction identified the presence of both $CaCO_3$ and CaO.

Table 19

X-RAY DIFFRACTION IDENTIFICATION OF PFBC RESIDUES

Sample	Separation	Chem Composition								
		$CaSO_4$	$CaSO_3$ Calcite	CaO	$Ca(OH)_2$	MgO	SiO_2	α Fe_2O_3	Fe_3O_4 Spinel	Others
Exxon 43.2/43.3 Bed Mat'l	General grind	Major	Minor	Minor		Minor				
Bed Mat'l	Black particles							Major	Trace	
Bed Mat'l	Tan OD, white ID	Major	Hi-minor			Hi-minor				
Bed Mat'l	Dark reddish OD	Minor	Trace				Major			
	Grey ID									
Bed Mat'l	Brown OD, white ID	Major	Hi-Minor	Hi-Minor						
Exxon 43.3 Carry-over	General grind	Hi-Minor				Trace	Major	Minor		
Exxon 45, Regenerative Comb. Bed Mat'l, Reg've	General grind	Major	Trace	Hi-Minor	Trace					
Comb. Bed Mat'l	Brown OD, white ID	Major	Minor	Hi-Minor	Trace		Trace			
Comb. Bed Mat'l	Brown OD, grey ID						Major			Trace
Exxon 45 Regenerative Bed Mat'l	Agglomerates - general grind		Trace	Major	Trace					Trace Ca_3SiO_5
Reg. Bed Mat'l	Agglomerates - brown glassy phase		Trace	Major	Trace					Trace Ca_3SiO_5
Reg. Bed Mat'l	Granular- - general grind	Major		Hi-Minor	Trace		Trace			
Reg. Bed Mat'l	Granular- - brown OD, white ID	Major		Major	Trace		Minor	Trace		
Reg. Bed Mat'l	Granular- - slag phase									Major Ca_3SiO_5
Exxon 45 Carry-over	General grind	Hi-Minor					Major	Minor		
Exxon 30.4 Bed Hydrated (via RS)	General grind	Minor	Major		Trace					
Exxon 30.4 Carry-over (via RS)	General grind	Minor					Major	Minor		Trace $Al_6Si_2O_{13}$
Exxon 43.5 Carry-over (via RS)	General grind	Minor		Possible			Major	Minor		
Exxon 67 Fines (3rd cyclone)	General grind	Hi-Minor					Major	Minor		

Exxon 45 is a run with sorbent regeneration, using limestone as the desulfurizing sorbent. The regenerator material is partially agglomerated; the agglomerates might have been formed during shutdown, when a temperature excursion occurred due to CaS oxidation. Because of the small amount of CaS present, X-ray diffraction patterns did not show CaS at all. Indeed, wet chemical analysis showed very low sulfide ($\leq$0.1%) in the regenerator bed material. Exxon 45 is not considered representative of the regenerative PFBC process. X-ray diffraction identified the agglomerated portion of the bed as primarily CaO (with little $CaSO_4$ or CaS), and with SiO_2 and Fe_2O_3 as minor species.

The Exxon 67 run was a 100-hr shakedown run for the DOE-funded material testing program on the EPA miniplant, in which boiler tube materials supplied by Westinghouse and gas turbine specimens supplied by the General Electric Company (GE) were exposed to FBC environments. In this run three stages of cyclones in series were used on the miniplant combustor flue gas in order to remove enough particulates to give a meaningful test of the gas turbine specimens. The solid residue Westinghouse obtained for the testing reported here is fine material collected by the third cyclone.* For comparison, the other Exxon carry-over material discussed in this report (from runs other than 67) is material collected by the second cyclone.*

In order to correlate the various EPA contractors' efforts in the area of FBC solid waste disposal, we requested and received samples from the Ralph Stone Company,[27] which had carried out a FBC solid waste program under contract to EPA. The samples obtained included the two PER residues discussed earlier and three Exxon residues (Exxon 43.5 bed, Exxon 30.4 bed, and Exxon 30.4 carry-over). Sample Exxon 30.4 bed had been hydrated and air dried prior to being sent to us.

In general, PFBC once-through bed material consists of major amounts of $CaSO_4$, minor amounts of $CaCO_3$ (sometimes CaO, depending on whether the temperature is high enough to calcine the calcium fraction), and minor-to-trace amounts of SiO_2, αFe_2O_3, and Fe_3O_4 spinel. Once-through PFBC bed usually contains less CaO (and more $CaCO_3$) than does AFBC bed material, which suggests a possibly significant difference in residue leaching/activity properties. Regenerative PFBC bed contains major $CaSO_4$ and CaO, and minor-to-trace SiO_2 and αFe_2O_3. PFBC carry-over has major SiO_2 and minor $CaSO_4$ and αFe_2O_3. The lighter particles consist mostly of sulfated and unsulfated limestone or dolomite ($CaSO_4$, $CaCO_3$, CaO, $Ca(OH)_2$, MgO). The darker particles are high in SiO_2, αFe_2O_3, Fe_3O_4, and other trace impurities.

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*These refer to third-stage and second-stage cyclones.

Leaching results using continuous and intermittent shake tests are summarized in Table 20. Leachate quality is similar for all four bed materials. Calcium, SO_4, TDS, and pH are major concerns. Dissolved calcium exhibited fluctuation because of carbonation by CO_2 in air; white $CaCO_3$ precipitate was crystallized on the leachate surface on exposure to air. This was especially true for the leachate of Exxon 45 regenerator bed agglomerate; like the one other residue that showed this precipitation tendency (the PER AFBC material discussed previously), the PFBC regenerator agglomerate contained CaO as a major species. The pH improved with time for carry-over leachate but remained unchanged for the bed material. Sulfate was relatively unchanged with time with the exception of leachate from Exxon 45 regenerator agglomerates, which were low in solid SO_4.

Finally, the leachate from the carry-over is not only superior initially; it also improves faster with time or total leachate volume passing from the sample. The results are not surprising in view of the lower CaO content of the carry-over; also, the probable pozzolanic reactions between the high SiO_2 content in coal ash and the CaO present in sorbent fines could serve to reduce leaching tendencies. The better leachate quality from the carry-over material is also shown in Figure 7, which plots specific conductance versus total leaching time or leachate volume.

Table 20

Dwg. 2621C22

LEACHATE CHARACTERISTICS OF PFBC RESIDUES

Residue	Chemical Characteristics	Intermittent Shake, no. of 72-hr Intervals															Continuous Shake	
		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	100 hr	200 hr
Ex. 43.2/43.3 Bed	pH	12.0	12.2	12.2	12.2	12.2	12.2	12.2	12.1	12.2	12.0	12.2	12.3	12.0	11.7	11.6	12.1	12.2
	Specific Conductance millimho/cm	8.04	8.01	7.60	7.97	7.43	7.89	7.48	8.10	7.47	7.68	7.48	6.14	4.65	3.92	3.59	8.56	8.43
	Ca, mg/ℓ	1136	1304	1328	1288	1216	1260	1192	1336	1224	1236	1176	840	876	708	704	1268	1304
	SO_4, mg/ℓ	1352	1352	1366	1225	1187	1213	1380	1445	1150	1366	1273	1175	1395	1380	1427	1325	1273
Ex. 43.3 Carry-over	pH	12.0	11.3	10.8	10.7	10.6	10.6	10.3	10.4	10.3	10.3	10.3	10.2	10.0	9.9	9.7	11.9	11.3
	S.C. millimho/cm	6.73	2.98	2.41	2.49	2.43	2.51	2.41	2.46	2.37	2.53	2.41	2.36	2.32	2.42	2.39	5.46	2.99
	Ca, mg/ℓ	888	672	664	656	640	656	656	672	656	676	672	708	676	736	720	924	672
	SO_4, mg/ℓ	1247	1352	1445	1410	1510	1366	1278	1445	1458	1445	1510	1529	1352	1460	1492	1247	1285
Ex. 43.5 Carry-over	pH	11.1	10.7	10.4	10.2	10.0	10.1	9.7	9.2	9.5	9.2	9.0	9.1	9.4	8.4	8.6	9.1	9.68
	S.C. millimho/cm	2.88	2.43	2.22	2.18	2.10	1.9	1.83	1.41	1.70	1.73	1.60	1.41	1.46	1.51	1.29	2.53	2.66
	Ca, mg/ℓ	648	648	620	588	600	552	548	500	440	448	412	376	392	368	320	824	720
	SO_4, mg/ℓ	1529	1353	1311	1187	1105	1139	1020	923	885	971	751	738	885	758	590	1583	1712
Ex. 30.4 Bed, Hydrated	pH	12.1	12.3	12.1	12.1	12.0	12.2	12.1	12.0	12.0	11.8	11.8	11.8	11.6	11.4	11.2	12.2	12.0
	S.C. millimho/cm	8.07	7.38	7.12	7.19	7.15	6.89	6.46	6.2	5.44	4.7	4.66	3.76	3.63	3.31	2.55	8.47	7.81
	Ca, mg/ℓ	1048	1056	964	1112	848	872	784	776	832	720	792	720	664	640	596	1056	1248
	SO_4, mg/ℓ	894	1225	1163	950	1040	1150	1030	1127	1150	1127	1105	1127	1380	1175	1083	1380	1236
Ex. 30.4 Carry-over	pH	10.1	10.1	10.1	9.9	9.9	9.7	9.2	9.4	8.9	8.6	8.3	8.2	7.9	7.9	7.9	10.0	9.53
	S.C. millimho/cm	2.4	2.24	2.16	2.22	2.21	2.16	2.10	1.99	2.05	2.12	1.99	1.97	2.02	1.92	1.57	2.26	2.55
	Ca, mg/ℓ	736	696	565	632	668	636	664	608	560	592	536	576	564	488	416	688	736
	SO_4, mg/ℓ	1510	1380	1260	1236	1273	1366	1260	1213	1200	1200	1150	1175	1225	1150	758	1353	1529
Ex. 45 Combustor Bed (regenerative)	pH	12.2	12.3	12.2	12.0	12.0	12.2	12.2	12.1	12.1	12.0	12.1	12.2	12.0	12.0	12.0	12.2	12.0
	S.C. millimho/cm	8.26	7.56	7.79	6.74	7.66	7.46	7.51	7.54	7.35	7.84	8.24	7.96	7.79	8.4	7.97	8.58	8.42
	Ca, mg/ℓ	1024	1104	1120	988	944	1000	1000	1000	1140	1104	1248	1288	1156	1144	1160	1200	1332
	SO_4, mg/ℓ	1325	1366	1445	1285	1116	1030	1200	1325	1339	1213	1200	1353	1352	1175	1325	1396	1352
	S, mg/ℓ	83	36	36	14	15	12	15	10	<10	<10	<10	<10	<10	<10	<10	53.3	42.1
Ex. 45 Reg'tor Bed (granular)	pH	12.2	12.3	12.2	12.0	12.0	12.2	12.2	12.1	12.1	12.1	12.1	12.2	12.0	12.0	12.0	12.2	12.0
	S.C. millimho/cm	8.59	7.85	7.91	7.79	7.69	7.60	7.77	7.77	7.44	8.17	8.33	8.02	8.05	8.5	8.11	8.65	8.32
	Ca, mg/ℓ	1024	1128	1056	984	908	968	1016	1064	1136	1120	1244	1284	1212	1164	1168	1288	1288
	SO_4 mg/ℓ	1366	1298	1188	1200	1071	1150	1182	1285	1311	1311	1187	1272	1380	1247	1235	1493	1352
	S, mg/ℓ	90	48	23	15	13	16	15	<10	<10	<10	<10	<10	<10	<10	<10	64.8	38.2
Ex. 45 Reg'tor Bed (agglomerated)	pH	12.2	12.3	12.2	12.0	12.0	12.2	12.2	12.2	12.1	12.1	12.1	12.2	12.0	12.0	12.0	12.3	12.0
	S.C. millimho/cm	8.05	7.33	7.57	7.34	7.19	7.0	6.95	7.04	7.01	7.57	7.59	7.33	7.61	8.06	7.59	8.46	7.68
	Ca, mg/ℓ	–	464	448	648	–	–	–	–	584	560	648	668	592	576	600	–	732
	SO_4, mg/ℓ	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10	<10
	S, mg/ℓ	23	19	14	11	13	14	15	<10	<10	<10	<10	<10	<10	<10	<10	21.0	14.0
Ex. 45 Carry-over	pH	11.8	10.9	10.6	10.2	10.1	10.1	9.8	9.3	9.7	9.5	9.4	8.5	9.2	7.9	9.1	12.0	10.4
	S.C. millimho/cm	3.93	2.62	2.38	2.28	2.23	2.06	2.0	1.89	1.95	1.90	1.86	1.76	1.85	2.0	1.7	5.6	2.62
	Ca, mg/ℓ	628	672	656	624	648	592	604	576	512	520	484	496	512	532	456	824	648
	SO_4, mg/ℓ	1380	1547	1325	1298	1213	1186	1225	1116	1071	1083	1010	1050	1188	1150	931	1510	1475
	S, mg/ℓ	49	34	44	18	23	23	20	12	13	<10	<10	<10	<10	<10	<10	45.2	27.3
Ex. 67 Carry-over (fines < 15 μm)	pH	8.5	8.3	8.1	8.0	8.0	7.9	7.9	7.7	7.6	7.5	–	–	–	–	–	–	8.0
	S.C. millimho/cm	19.7	7.72	3.58	2.52	2.23	2.14	2.08	2.11	2.05	2.09	–	–	–	–	–	–	9.16
	Ca, mg/ℓ	424	428	516	608	616	616	584	608	604	576	–	–	–	–	–	–	488
	Mg, mg/ℓ	5582	1538	358	125	53	24	24	14	19	31	–	–	–	–	–	–	1273
	SO_4	20400	6025	2210	1583	1645	1353	1285	1285	1410	1380	–	–	–	–	–	–	6975

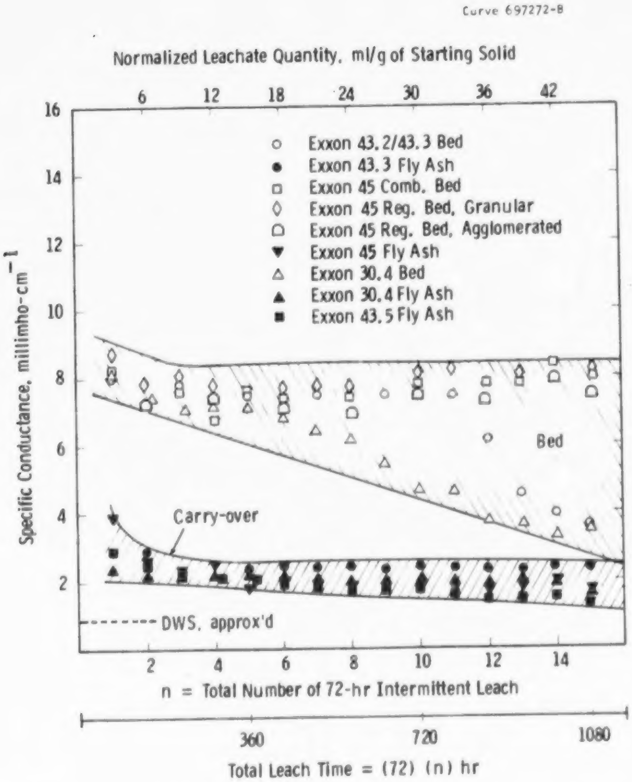

Figure 7 - Leachate Quality of PFBC Residues as a Function of Intermittent Leaching

Trace elements in PFBC leachates which had been investigated more extensively than the AFBC leachate in the previous report[5] are presented here again for several of the Exxon PFBC residues, with and without sorbent regeneration, in Tables 21 and 22. Other solid and leachate characteristics are also summarized, including major and minor species, pH, specific conductance, and TOC in the leachate. As expected from the previous findings, all trace metal elements were lower than the DWS except for one, barium in the leachate of the agglomerated portion of the Exxon 45 regenerator bed material. This is not of great concern because agglomeration would not be expected in a typical run. The TOC was low for all; calcium, SO_4, pH, specific conductance were high, as previously reported.

Table 21

Dwg. 1709B89

SOLID AND LEACHATE CHARACTERISTICS OF PFBC RESIDUE FROM EXXON
(200-hr Continuous Shake Test)

Substance	PFBC Solid, Wt %[a]			PFBC Leachate, mg/ℓ[a]			DWS,[b] mg/ℓ
	(1)	(2)	(3)	(1)	(2)	(3)	
Al	> 10	> 10	> 10	< 0.05	< 0.05	< 0.05	
Ag				< 0.01	< 0.01	< 0.01	0.05
As	0.005	0.003	0.003	0.002	0.019	0.013	0.05
B	0.01	0.02	0.02	0.2	0.2	0.5	
Ba				< 1	< 1	< 1	1.0
Be	0.0001	0.0003	0.0003	< 0.01	< 0.01	< 0.01	
Bi	< 0.0003	< 0.0003	< 0.0003	< 0.01	< 0.01	< 0.01	
Ca	35.04	5.76	4.56	1,248	736	720	200
Cd	< 0.003	< 0.003	< 0.003	< 0.01	< 0.01	< 0.01	0.01
Co	0.001	0.001	0.001	< 0.05	< 0.05	< 0.05	
Cr	0.003	0.003	0.003	< 0.05	< 0.05	< 0.05	0.05
Cu	0.005	0.01	0.01	< 0.05	< 0.05	< 0.05	1.0
Fe	> 10	> 10	> 10	< 0.1	< 0.1	< 0.1	0.3
Hg				< 0.001	< 0.001	< 0.001	0.002
Mg	1.15	0.67	3.02	14.4	< 5	28.8	150
Mn	0.01	0.01	0.01	< 0.05	< 0.05	< 0.05	0.05
Mo	0.001	0.002	0.002	0.05	0.1	0.2	
Na	0.1	0.1	0.1	5	< 5	> 5	
Ni	0.01	0.01	0.01	< 0.05	< 0.05	< 0.05	2.0
Pb	0.005	0.005	0.005	< 0.05	< 0.05	< 0.05	0.05
Sb				< 0.05	< 0.05	< 0.05	
Se				< 0.003	< 0.003	< 0.003	0.01
Si	> 10	> 10	> 10	0.5	< 0.05	< 0.05	
Sn	< 0.0003	< 0.0003	< 0.0003	< 0.05	< 0.05	< 0.05	1.0
Sr				5	> 5	> 5	
Ti	0.1	0.2	0.2	< 0.05	< 0.05	< 0.05	
V	0.001	0.003	0.003	< 0.05	0.1	0.05	
Zn	0.01	0.01	0.01	< 1	< 1	< 1	5.0
Zr	0.01	0.01	0.01	< 0.1	< 0.1	< 0.1	
SO_4	38.72	30.56	40.64	1,236	1,528	1,712	250
TOC				< 10	< 10	< 10	
pH				12.03	9.53	9.68	6.5 to 9.2
SC, μmho/cm				7,810	2,550	2,660	~ 750

[a] (1) Exxon 30.4 Bed, Hydilated and Dried
(2) Exxon 30.4 Carry-over
(3) Exxon 43.5 Carry-over

[b] DWS: NIPDWR, USPHS, and WHO drinking water standards.

▨ exceeds DWS

Table 22 Dwg. 2624C72

SOLID AND LEACHATE CHARACTERISTICS OF PFBC RESIDUES WITH SORBENT REGENERATION

(200-hr Continuous Shake Test)

Substance	Solid Analysis, Wt %[a]				Leachate Analysis, mg/ℓ[a]				DWS,[b] mg/ℓ
	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)	
Al	> 10	>> 10	>> 10	> 10	< 0.05	0.5	< 0.05	0.1	
Ag	< 0.0001	< 0.0001	< 0.0001	< 0.0001	< 0.01	< 0.01	< 0.01	< 0.01	0.05
As	< 0.01	< 0.01	< 0.01	< 0.01	< 0.002	< 0.005	< 0.002	0.002	0.05
B	0.08	0.05	0.08	0.01	0.3	0.3	0.2	2.0	
Ba					< 1	< 1	< 1	▨ > 1	1.0
Be	0.0003	0.001	0.0003	< 0.0001	< 0.01	< 0.01	< 0.01	< 0.01	
Bi	< 0.0033	< 0.0033	< 0.0033	< 0.0033	< 0.01	< 0.01	< 0.01	< 0.01	
Ca	31.2	11.04	32	51.36	▨ 1,332	▨ 648	▨ 1,288	▨ 732	200
Cd	< 0.0005	< 0.0005	< 0.0005	< 0.0005	< 0.01	< 0.01	< 0.01	< 0.01	0.01
Co	< 0.003	< 0.003	< 0.003	0.005	< 0.05	< 0.05	< 0.05	< 0.05	
Cr	0.005	0.005	0.005	0.005	< 0.05	< 0.05	< 0.05	< 0.05	0.05
Cu	0.006	0.006	0.003	< 0.001	0.2	< 0.05	< 0.05	< 0.05	1.0
Fe	> 10	> 10	> 10	> 10	< 0.1	< 0.1	< 0.1	< 0.1	0.3
Hg					< 0.001	< 0.001	< 0.001	< 0.001	0.002
Mg	0.76	0.8	0.9	1.3	24	< 5	< 5	21.6	150
Mn	0.03	0.03	0.03	0.03	< 0.05	< 0.05	< 0.05	< 0.05	0.05
Mo	0.001	0.003	0.001	< 0.001	0.1	0.2	0.05	< 0.05	
Na	< 0.1	> 1	< 0.1	< 0.1	< 5	> 5	< 5	< 5	
Ni	0.005	0.005	0.005	0.005	< 0.05	< 0.05	< 0.05	< 0.05	2.0
Pb	< 0.001	0.005	< 0.001	< 0.001	< 0.05	< 0.05	< 0.05	< 0.05	0.05
Sb	< 0.01	< 0.01	< 0.01	< 0.01	< 0.05	< 0.05	< 0.05	< 0.05	
Se					< 0.003	< 0.003	< 0.003	< 0.003	0.01
Si	>> 10	>> 10	>> 10	>> 10	0.5	> 5	0.5	0.5	
Sn	0.001	0.001	0.001	0.001	< 0.05	< 0.05	< 0.05	< 0.05	1.0
Sr					> 5	> 5	> 5	> 5	
Ti	0.1	0.5	0.3	0.1	< 0.05	< 0.05	< 0.05	< 0.05	
V	0.005	0.01	0.005	0.003	< 0.05	0.1	< 0.05	< 0.05	
Zn					< 1	< 1	< 1	< 1	5.0
Zr	0.003	0.03	0.005	0.001	< 0.1	< 0.1	< 0.1	< 0.1	
SO_4	27.45	14.5	21.6	1.8	▨ 1,352	▨ 1,475	▨ 1,352	0	250
$S^=$	0.07	0.1	0.06	0.06	42	27.3	38	14	
TOC					< 10	< 10	< 10	< 10	
pH					▨ 11.98	▨ 10.4	▨ 12.02	▨ 12.03	6.5 to 9.2
SC, μmho/cm					▨ 8,420	▨ 2,620	▨ 8,320	▨ 7,680	~ 750

[a] (1) Exxon No. 45 combustor bed
(2) Exxon No. 45 carry-over
(3) Exxon No. 45 regenerator (granular)
(4) Exxon No. 45 regenerator (agglomerated)

[b] DWS: NIPDWR, USPHS, and WHO drinking water standards.

▨ exceeds DWS

The Exxon 67 sample, which was collected from the third cyclone, was much finer than the other batches of carry-over tested. These third-cyclone fines represent the material that passed uncaptured through the second cyclone; the Exxon carry-over for the other tests reported here is material captured by the second cyclone. The particle size distribution of the Run 67 fines is shown in Table 23. The SEM and EDAX spectrum (Figure 8) shows that the physical appearance and elemental distribution of Exxon 67 fines are similar to those of a previously tested PFBC stack particulate sample obtained after the second cyclone of Exxon 34.[5,34] Cenospheres are lacking in both ash samples. The similarity between the third-cyclone catch and the post-second-cyclone flue gas particulate sample is, of course, exactly what would be expected.

Both the continuous and the intermittent leach methods were employed on the Exxon 67 sample; results are shown in Tables 20 and 24 and in Figure 8. The leaching property with deionized water was found to be different from the other FBC solids tested previously in several areas:

- Magnesium leachability - The high magnesium concentration in the leachate (Table 23), which decreased rapidly with total leachate volume passing through the sample (Figure 8), contrasts with the previous results, which indicated that magnesium did not leach out, even from spent dolomite sorbent. After several intermittent shakes, the magnesium concentration fell to the low levels typical of previous results (Figure 8).

Table 23

PARTICLE SIZE DISTRIBUTION OF EXXON 67 THIRD CYCLONE FINES

Weight, %	5	10	25	50	75	90	95
Size less than, μm	1.33	1.73	2.65	4.75	8.30	12.50	15.70

Table 24

Dwg. 2618C86

CHEMICAL CHARACTERISTICS OF EXXON 67 THIRD CYCLONE FINES AND THEIR LEACHATE (200-hr Continuous Shake Test)

Substance	Solid, ppm	Leachate, mg/ℓ		DWS, mg/ℓ
		Deionized Water, pH ≃ 7.0	Acetate Buffer, pH ≃ 4.5	
Aℓ	25.4%	<1	1	
Ag	<1	<0.01	<0.01	0.05
As		0.01	0.002	0.05
B	300	2	1	
Ba	500	<1	<1	1.0
Be	15	<0.01	<0.01	
Bi	<1	<0.01	<0.01	
Ca	7.2%	▨ 488	▨ 536	200
Cd	3	<0.01	▨ 0.1	0.01
Co	10	<0.04	0.1	
Cr	200	0.03	0.03	0.05
Cu	30	<1	<1	1.0
Fe	5.53%	▨ 0.4	0.3	0.3
Hg		0.0009	0.0007	0.002
K	1.16%			
Mg	3.84%	▨ 1672	▨ 2016	150
Mn	330	▨ 0.24	▨ 0.7	0.05
Mo	30	2	0.2	
Na	0.59%			
Ni	150	<1	<1	2.0
Pb	30	<0.02	<0.02	0.05
Sb	<33	<0.5	<0.5	
Se		▨ 0.03	<0.001	0.01
Si	15.4%	5	> 10	
Sn	<5	<0.2	<0.2	1.0
Ti	> 1000	<0.2	<0.2	
V	200	0.15	<0.05	
Zn	500	4	<4	5.0
Zr	500	<1	<1	
SO_3		<10	<10	
SO_4	22.23%	▨ 6975	▨ 7575	250
S=	<0.05%	<10	<10	
F	<0.02%	▨ 6	<1	2.4
Cl	0.14%	10	<1	250
Br		<1	<1	
NO_2		<1	<10	
NO_3 (as N)		<1	<1	10
PO_4	0.25%	<1	<1	
Free C	1.2%			
TOC		<20		
pH		8.02	▨ 4.7	6.5 to 9.2
SC (μmho/cm)		▨ 9160	▨ 13000	~750

DWS — NIPDWR, USPHS and WHO Drinking Water Standards

▨ Exceed DWS

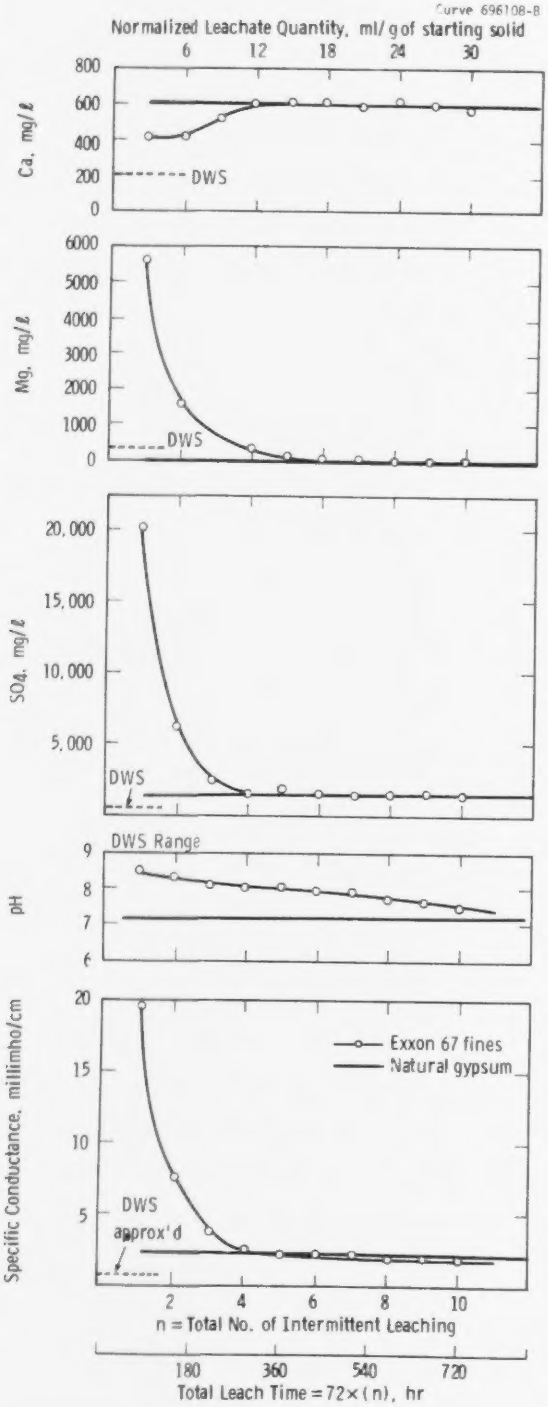

Figure 8 - Leachate Characteristics of Exxon 67 Third Cyclone Particulates as a Function of Intermittent Leaching

- SO_4 concentration - The sulfate concentrations in the previous FBC leachates were similar to those in the natural gypsum leachate and were dominated by $CaSO_4$ solubility, but in the Exxon 67 leachate SO_4 was 5 to 15 times higher. The high SO_4 decreased rapidly with the total leachate volume passing through the sample and with total leaching time. After four 72-hr cycles, the Exxon 67 leachate SO_4 equilibrated to within the previous SO_4 range, which appeared to be controlled by $CaSO_4$ solubility (Figure 8).
- Specific Conductance - The total dissolved solids as estimated by specific conductance were also higher in the Exxon 67 leachate than in the previous carry-over materials. Like calcium, magnesium, and SO_4, the TDS settled down much like natural gypsum leachate after four 72-hr leach cycles (Figure 8).
- Calcium solubility - The calcium solubility seemed to be suppressed initially when magnesium and SO_4 concentrations were high but increased to be dominated by $CaSO_4$ solubility when magnesium was depleted after four cycles (Figure 8).
- pH - The initial leachate pH from Exxon 67 fines was lower than most FBC carry-over leachate pH (∿9 to 10), possibly because of the lower CaO content of this material.
- Trace elements - Unlike the previous findings, several trace elements (manganese, selenium, fluorine, and iron) exceeded the DWS, as shown on Table 24, with deionized water leaching. This increase could be due to the lower leachate pH.

The higher magnesium, SO_4, and TDS in the initial leachate suggested the presence of a highly soluble species, $MgSO_4$ or $CaSO_4 \cdot 3MgSO_4$. ANL[20] has reported the presence of $CaSO_4 \cdot 3MgSO_4$ in some FBC sorbent. The chemical analysis of the Exxon 67 carry-over solid also suggested the presence of other sulfate in addition to $CaSO_4$ because the SO_4-to-calcium molar ratio was greater than 1 ($SO_4/Ca = 1.3$). X-ray diffraction, however, showed the presence of neither the magnesium salt suggested above nor any other sulfate (in addition to $CaSO_4$), so that if any sulfate salts were present in addition to $CaSO_4$, the concentrations were lower.

Leaching tests were also conducted on Exxon 67 residue using sodium acetate/acetic acid buffer with pH = 4.4 and specific conductance 3.31 millimho/cm, as suggested by the ASTM proposed leaching method[28] to simulate an inhomogeneous landfill site where codisposal of municipal and industrial waste often results in acidic leaching conditions. In addition, at the time these tests were conducted, it was known that EPA was considering an acetate/acetic acid shake test in order to determine whether a waste should be considered hazardous under RCRA because of toxicity.

Note from Table 24 that leaching with a lower pH medium had the following effect on the resultant leachates:

- Aluminum, calcium, cadmium, magnesium, manganese, silicon, SO_4, and TDS increased with decreasing pH. One would expect that the more acidic leaching medium might tend to dissolve the alkaline calcium-containing residue, thus exacerbating the leaching of components out of the residue.
- Arsenic, boron, selenium, vanadium, zinc, fluorine, chlorine, and pH of the resultant leachate decreased with decreasing pH.

Leaching with an acidic medium is discussed further in a later section, "Leaching Medium Effect on Leachate."

The residual heat-release property of Exxon 67 fines (discussed in a later section) falls into the range of the FBC carry-over materials investigated previously.

The leaching property of the PFBC Exxon 67 third-cyclone particulate indicated the need for further tests on FBC carry-over, particularly fines of less than 15 μm in size. Previous AFBC materials from a MERC run have also shown that although the major species are lower in the leachate of the carry-over material, trace elements increase both in the solid and the leachate with decreasing particle size.

Combustion Power Residue[26]

The CPU-400 Process Development Unit (PDU) was originally constructed for EPA at Combustion Power Co. to convert the heat energy of municipal solid waste to electrical energy by using a fluid-bed combustor/gas turbine cycle. The pressurized fluidized-bed combustor on the CPU-400 unit is called an adiabatic combustor because no heat transfer surface is immersed in the bed; rather, bed temperature is controlled by using high levels of excess air (∿300% excess) in the combustor. More recently, the facility has been used under DOE funding to demonstrate the viability of the direct coal-fired gas-turbine approach based on CPU-400 technology. The P-403 run was a 175-hr test in the CPU-400 at 405.2 kPa (4 atm) pressure and 855°C. Illinois No. 6 coal and Kaiser dolomite were used. Burgess No. 10 pigment (aluminum silicate) was fed with the coal-dolomite mix at a rate of 0.4 percent by weight of the coal feed as a corrosion inhibitor. Note that the P-403 sample tested here is an aged sample (>2 years old); for this reason -- as well as because of the use of the pigment -- the samples may not represent typical residue from the adiabatic PFBC system.

The residue sample obtained from run P-403 was carry-over material collected in a baghouse. Both physical and morphological characteristics were investigated. The particle size ranged between <1 and 40 μm. Figure 9 shows a SEM photomicrograph of P-403 carry-over and its EDAX spectra scanned over the entire area and three specific locations. The area-scan EDAX analysis (Figure 9b) indicated the presence of calcium, silicon, sulfur, magnesium, and potassium, in decreasing order.

The bright particle shown at Site A is found to consist of $CaSO_4$, SiO_2, MgO, and Fe_2O_3 (Figure 9c). The dark particle shown at Site B contains mostly unsulfated $CaCO_3$ or CaO (Figure 9d). Another dark area at Site C shows $CaSO_4$ predominantly (Figure 9e).

The leaching property of P-403 ash was investigated, employing both the continuous and intermittent shake procedure. Table 25 and Figure 10 summarize the results. Leachate of the P-403 ash from the adiabatic combustor showed chemical characteristics similar to those of the nonadiabatic PFBC ash from the standpoint of leaching of major calcium species.

The P-403 leachate had low TOC. The trace metal elements among other chemical characteristics in the solid and its leachate are summarized in Table 25. The P-403 leachate met the drinking water standards for those elements where standards exist. Although there is no drinking water standard for boron, it should be noted that the P-403 ash leachate had a boron concentration of more than 5 ppm. The EPA-recommended criterion for boron for long-term irrigation on sensitive crops is 0.75 ppm. The recommended maximum concentration for long-term irrigation for tolerant plants is 2 ppm. For shorter periods of time, higher concentrations are acceptable.

Processed FBC Residue Characterization and Leachate

As discussed in the previous Westinghouse report to EPA[5] and Section 8 of this report, Westinghouse is investigating the means for reducing the environmental impact of FBC residue disposal. One option, which has received the most attention, is the fixation of FBC spent sorbent/carry-over mixtures at room temperature. The basis for this effort is that, upon exposure to water, mixtures of FBC spent sorbent and fly ash tend to set up as a cementlike mass. For more complete discussions on spent sorbent processing (i.e., fixation), refer to Section 8 of this report as well as to the previous Westinghouse report to EPA.*[5]

As part of the laboratory leaching studies described in this chapter, continuous and intermittent shake tests were conducted on samples of fixed material produced as described in the previous Westinghouse report

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*Pages 123-135 of Reference 17 describe the preparation of these samples. Note, however, that the caption of Table 34, p. 128, should refer to Exxon Run 27, not 43.

Dwg. 1709B92

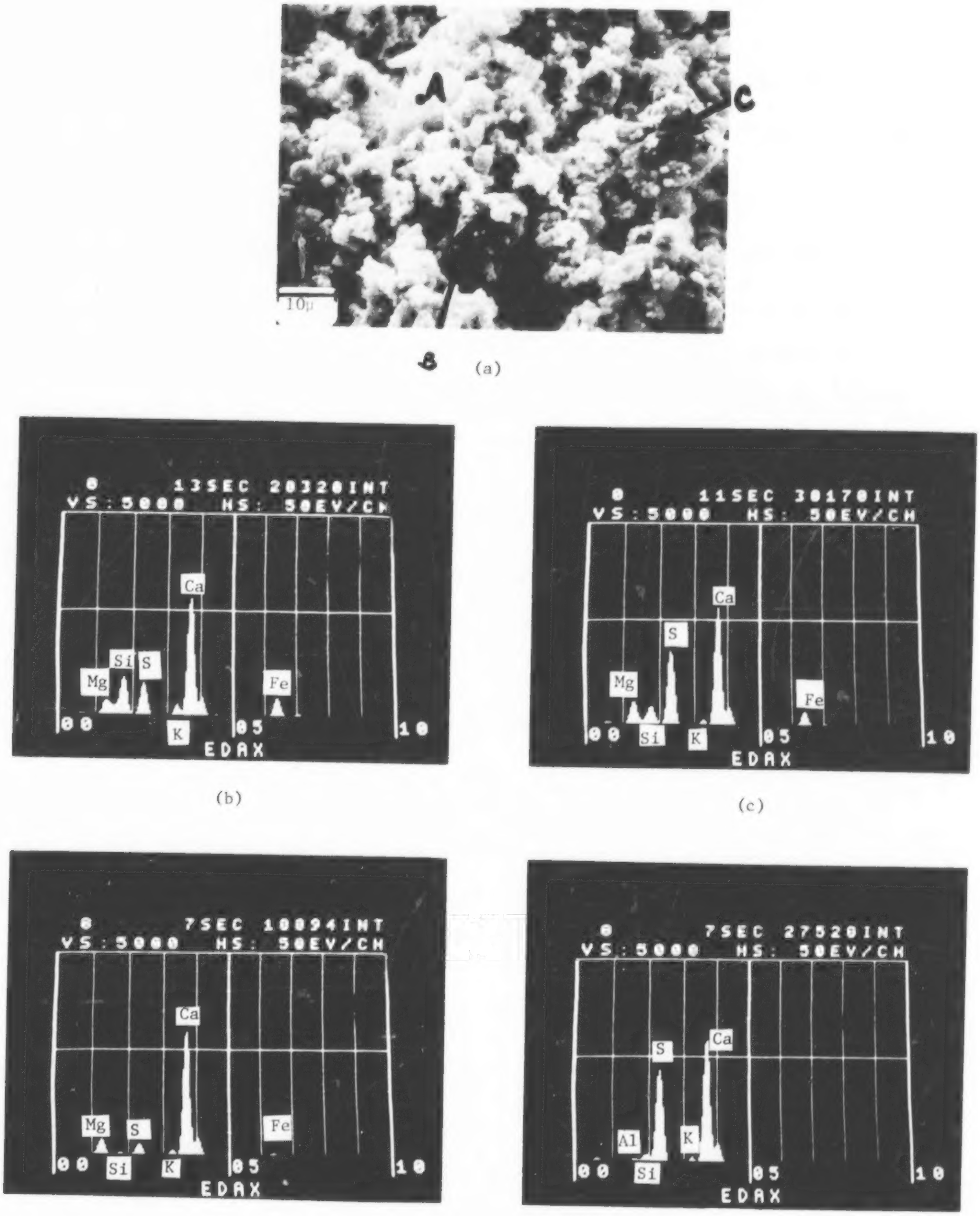
Table 25

SOLID AND LEACHATE CHARACTERISTICS OF ADIABATIC PFBC BAGHOUSE RESIDUE FOR COMBUSTION POWER CP-403 RUN

Substance	Solid, ppm	Leachate, mg/ℓ	DWS,[a] mg/ℓ
Al	Major	2	
Ag	< 1	< 0.01	0.05
As		< 0.003	0.05
B	500	> 5	
Ba		< 1	1.0
Be		< 0.01	
Bi	< 10	< 0.01	
Ca	16%	696	200
Cd	< 3	< 0.01	0.01
Co	15	< 0.01	
Cr	100	< 0.02	0.05
Cu	100	< 0.05	1.0
Fe	Major	< 0.05	0.3
Hg		< 0.002	0.002
Mg	8.7%	0	150
Mn	220	< 0.01	0.05
Mo	50	0.2	
Na	> 1,000	> 5	
Ni	80	< 0.05	2.0
Pb	50	< 0.01	0.05
Sb	< 33	< 0.01	
Se		< 0.003	0.01
Si	Major	> 4	
Sn	< 10	< 0.01	1.0
Sr	100	> 10	
Ti	> 1,000	< 0.05	
V	60	0.02	
Zn	150	< 1	5.0
Zr		< 1	
SO_4	18.5%	1,813	250
$S^=$	0.02%	< 5	
TOC		< 10	
pH		10.8	6.5 to 9.2
SC, μmho/cm		3,770	~ 750

[a] DWS - NIPDWR, USPHS, and WHO drinking water standards

▨ exceeds DWS



(a)

(b)

(c)

(d)

(e)

Figure 9 - Morphological Characteristics of CP-P403 Ash: (a) Typical SEM Photomicrograph, (b) Area-Scan EDAX Spectrum, (c) EDAX on Site A, (d) EDAX on Site B, (e) EDAX on Site C

Curve 691327-B

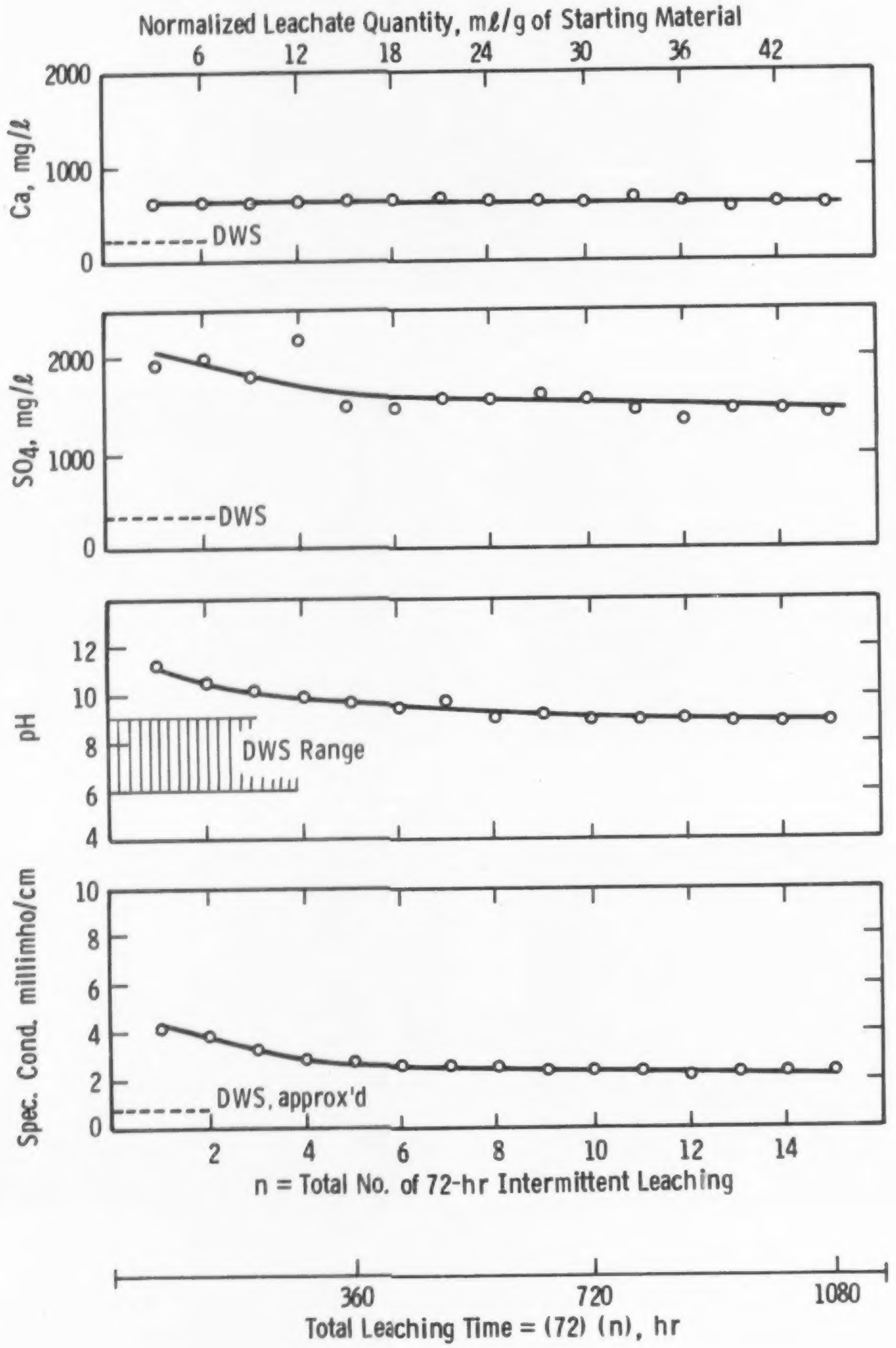


Figure 10 - Leachate Characteristics of CPU-400 P403 Ash from Combustion Power as a Function of Intermittent Leaching

to EPA.[5] These shake tests were to identify how effectively this low-temperature fixation reduced leaching properties. Among the fixation parameters investigated were the sorbent/ash-mixing ratio, water content, and air-curing time. Table 26 summarizes the samples studied. All are 5-cm cubes unless otherwise stated. Unprocessed spent bed material, carry-over (ash), an 80/20 bed/carry-over (sorbent/ash) mixture and gypsum were tested for comparison. The operating conditions of Exxon 27 runs from which the starting materials (FBC residues) were produced are presented in Table 8 of this report. Note that in the work reported here the only fly ash mixed with the spent bed material was carry-over from the same PFBC miniplant run that produced the spent bed material used in these tests. Work has also been carried out to investigate means for increasing the strength of the fixed residue by using fly ash generated in high-temperature conventional coal boilers; use of conventional boiler fly ash was not considered in this study.

Tables 27 through 30 summarize the leaching results on the 5-cm-cube compacts; all samples were leached as uncrushed cubes unless specified otherwise. On the basis of limited data points, no definite correlation was found between leaching property and compact processing parameters (sorbent/ash ratio, water content, and curing time). The initial leachates displayed some variation among different compacts, including identically processed cubes from different batches (II4D and II4D'). After five repeated, 72-hr shakes, the leachate quality of all compacts fell within the same range, which was superior to that from natural gypsum. The leachate quality from the 1080-hr continuous shake of all the compacts reached the level of gypsum leachate except that the compacts had a slightly higher pH.

Figure 11 compares the chemical characteristics of the leachate from processed sorbent/ash compact (I4D') prepared from Exxon 27 residues, the leachate of crushed powder from a similar compact (I4C'), and the leachate from an unprocessed bed/carry-over mixture (without being fixed: cast/cured). Although the spent bed/carry-over ratio (80/20) of the latter unprocessed mixture was different from that (64/36) of the processed compacts I4D' and I4C', the comparison is meant to show general

Table 26

Dwg. 2612C19

SUMMARY OF LEACHING TEST METHODS APPLIED TO THE EXXON 27 SORBENT/ ASH COMPACTS AND UNPROCESSED SORBENT/ASH AND MIXTURES
(Solids from EPA's PFBC Miniplant at Exxon)

Sample	Description	Leaching Method
I 1C	Wt ratio fly ash/total solid = 0.358 Wt ratio H_2O/total solid = 0.445 Air cured 7 days	1242-hr continuous shake, wt ratio solid/water = 1/10
I 1D	Same as I 1C	15 × 72-hr intermittent shake, wt ratio solid/water = 1/3
I 2C	Wt ratio fly ash/total solid = 0.358 Wt ratio H_2O/total solid = 0.445 Air cured 11 days	1080-hr continuous shake, wt ratio solid/water = 1/10
I 2D	Same as I 1C	15× 72-hr intermittent shake, wt ratio solid/water = 1/3
I 3C	Wt ratio fly ash/total solid = 0.358 Wt ratio H_2O/total solid = 0.445 Air cured 28 days	1080-hr continuous shake, wt ratio solid/water = 1/10
I 3D	Same as I 3C	15 × 72-hr intermittent shake, wt ratio solid/water = 1/3
I 4C'	Wt ratio fly ash/total solid = 0.100 Wt ratio H_2O/total solid = 0.445 Air cured 60 days	15 × 72-hr intermittent shake compact crushed to powder, wt ratio solid/water = 1/3
I 4D'	Same as I 4C'	15 × 72 hr intermittent shake, original cube (uncrushed), wt ratio solid/water = 1/3
II 1C	Wt ratio fly ash/total solid = 0.100 Wt ratio H_2O/total solid = 0.300 Air cured 7 days	1224-hr continuous shake, wt ratio solid/water = 1/10
II 1D	Same as II 1D	15 × 72-hr intermittent shake, wt ratio solid/water = 1/3
II 3C	Wt ratio fly ash/total solid = 0.100 Wt ratio H_2O/total solid = 0.300 Air cured 28 days	1080-hr continuous shake, wt ratio solid/water = 1/10
II 3D	Same as II 3C	15 × 72-hr intermittent shake wt ratio solid/water = 1/3
II 3E	Wt ratio fly ash/total solid = 0.100 Wt ratio water/total solid = 0.445 Air cured 28 days	1080-hr continuous shake, wt ratio solid/water = 1/10
II 3F	Same as II 3E	15 × 72-hr intermittent shake, wt ratio solid/water = 1/3
II 4C	Wt ratio fly ash/total solid = 0.100 Wt ratio water/total solid = 0.300 Air cured 60 days	1080-hr continuous shake, wt ratio solid/water = 1/10
II 4D	Same as II 4C	15 × 72-hr intermittent shake, wt ratio solid/water = 1/3
II 4C'	Same as II 4C	15 ×72-hr intermittent shake, compact crushed to powder, wt ratio solid/water = 1/3
II 4D'	Same as II 4C	15 × 72 hr intermittent shake, original cube (uncrushed), wt ratio solid/water = 1/3
III 2C	Wt ratio fly ash/total solid = 0.15 Wt ratio H_2O/total solid = 0.3 Air cured 21 days	1080-hr continuous shake, wt ratio solid/water = 1/10
III 2D	Same as III 2C	15 × 72-hr intermittent shake, wt ratio solid/water = 1/3
Exxon 19.6 Bed Material	Unprocessed (Spent limestone)	15 × 27-hr intermittent shake, wt ratio solid/water = 1/3
Exxon 19.6 Fly Ash	Unprocessed	Same as above
Exxon 27 Sorbent/Ash Mixture	Wt ratio Bed/ash = 80/20, Unprocessed mixture	Same as above
Gypsum	Natural	Same as above

Table 27

Dwg. 2612C20

SPECIFIC CONDUCTANCE OF LEACHATE FROM THE EXXON 27 SORBENT/ASH COMPACTS

Sample	Specific Conductance, millimho/cm															
	Intermittent Shake, no. of 72 hr Intervals															1080 hr. Cont's Shake
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
I 1C																2.55
I 1D	2.58	2.38	2.06	1.77	1.52	1.42	1.12	1.01	1.17	0.98	0.99	0.74	0.9	0.85	0.82	
I 2C																2.57
I 2D	2.43	2.08	1.66	1.45	1.57	1.14	1.08	1.05	0.97	1.06	1.13	1.06	1.00	0.91	0.93	
I 3C																2.72
I 3D	2.32	2.18	1.85	1.60	1.75	1.66	1.43	1.30	1.20	1.18	1.01	1.01	1.06	0.93	0.89	
I 4C' (crushed)	3.43	2.81	2.26	2.35	2.11	2.13	2.01	1.82	1.77	1.77	1.73	1.55	1.51	1.63	1.62	
I 4D'	2.93	1.85	1.43	1.43	1.34	1.24	1.21	1.16	1.23	1.19	1.12	1.05	0.99	1.15	1.14	
II 1C																2.23
II 1D	2.74	1.75	1.81	1.42	1.25	1.06	1.20	1.11	1.08	1.29	1.20	1.17	1.05	1.00	0.77	
II 3C																2.16
II 3D	5.17	3.17	1.92	1.63	1.74	1.41	1.21	1.07	0.83	0.82	0.84	0.76	0.73	0.72	0.72	
II 3E																2.25
II 3F	4.84	3.46	2.92	2.12	4.44	1.71	1.63	1.39	1.13	1.16	1.14	1.11	1.10	1.10	1.05	
II 4C																2.37
II 4D	2.59	2.68	1.67	1.47	1.20	1.12	1.41	0.92	0.88	0.83	0.95	0.85	1.07	0.90	0.86	
II 4C' (crushed)	7.31	4.9	3.96	3.32	2.62	2.62	2.25	1.98	2.00	1.82	1.78	1.65	1.63	1.50	1.50	
II 4D'	3.59	2.88	1.97	1.39	1.05	1.09	1.10	0.87	0.85	0.83	0.81	0.94	0.74	0.62	0.57	
III 2C																2.10
III 2D	4.32	2.12	1.65	1.36	1.21	1.19	0.81	0.88	1.03	0.88	0.97	0.8	0.86	0.93	0.85	
Unprocessed Exxon 19.6 Bed	8.29	8.50	7.90	7.86	7.17	6.52	6.11	3.97	3.09	2.43	2.45	2.30	2.21	1.82	1.92	
Unprocessed Exxon 19.6 Fly Ash	4.09	2.28	2.04	1.88	1.64	1.70	1.58	1.54	1.21	1.25	1.23	1.22	1.10	0.75	0.83	
Unproc. Exxon 27 Sorbent/Ash Mixture (80/20)	7.93	7.13	2.95	2.66	2.27	2.27	2.33	2.40	2.19	2.07	2.33	2.27	2.23	1.87	1.95	
Gypsum	2.12	2.21	2.09	2.08	1.96	2.08	2.10	2.12	2.05	1.91	2.12	2.16	2.12	2.08	1.96	

Table 27

Dwg. 2612C20

SPECIFIC CONDUCTANCE OF LEACHATE FROM THE EXXON 27 SORBENT/ASH COMPACTS

Sample	Specific Conductance, millimho/cm															
	Intermittent Shake, no. of 72 hr Intervals															1080 hr. Cont's Shake
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
I 1C																2.55
I 1D	2.58	2.38	2.06	1.77	1.52	1.42	1.12	1.01	1.17	0.98	0.99	0.74	0.9	0.85	0.82	
I 2C																2.57
I 2D	2.43	2.08	1.66	1.45	1.57	1.14	1.08	1.05	0.97	1.06	1.13	1.06	1.00	0.91	0.93	
I 3C																2.72
I 3D	2.32	2.18	1.85	1.60	1.75	1.66	1.43	1.30	1.20	1.18	1.01	1.01	1.06	0.93	0.89	
I 4C' (crushed)	3.43	2.81	2.26	2.35	2.11	2.13	2.01	1.82	1.77	1.77	1.73	1.55	1.51	1.63	1.62	
I 4D'	2.93	1.85	1.43	1.43	1.34	1.24	1.21	1.16	1.23	1.19	1.12	1.05	0.99	1.15	1.14	
II 1C																2.23
II 1D	2.74	1.75	1.81	1.42	1.25	1.06	1.20	1.11	1.08	1.29	1.20	1.17	1.05	1.00	0.77	
II 3C																2.16
II 3D	5.17	3.17	1.92	1.63	1.74	1.41	1.21	1.07	0.83	0.82	0.84	0.76	0.73	0.72	0.72	
II 3E																2.25
II 3F	4.84	3.46	2.92	2.12	4.44	1.71	1.63	1.39	1.13	1.16	1.14	1.11	1.10	1.10	1.05	
II 4C																2.37
II 4D	2.59	2.68	1.67	1.47	1.20	1.12	1.41	0.92	0.88	0.83	0.95	0.85	1.07	0.90	0.86	
II 4C' (crushed)	7.31	4.9	3.96	3.32	2.62	2.62	2.25	1.98	2.00	1.82	1.78	1.65	1.63	1.50	1.50	
II 4D'	3.59	2.88	1.97	1.39	1.05	1.09	1.90	0.87	0.85	0.83	0.81	0.94	0.74	0.62	0.57	
III 2C																2.10
III 2D	4.32	2.12	1.65	1.36	1.21	1.19	0.81	0.88	1.03	0.88	0.97	0.8	0.86	0.93	0.85	
Unprocessed Exxon 19.6 Bed	8.29	8.50	7.90	7.86	7.17	6.52	6.11	3.97	3.09	2.43	2.45	2.30	2.21	1.82	1.92	
Unprocessed Exxon 19.6 Fly Ash	4.09	2.28	2.04	1.88	1.64	1.70	1.58	1.54	1.21	1.25	1.23	1.22	1.10	0.75	0.83	
Unproc. Exxon 27 Sorbent/Ash Mixture (80/20)	7.93	7.13	2.95	2.66	2.27	2.27	2.33	2.40	2.19	2.07	2.33	2.27	2.23	1.87	1.95	
Gypsum	2.12	2.21	2.09	2.08	1.96	2.08	2.10	2.12	2.05	1.91	2.12	2.16	2.12	2.08	1.96	

Table 28

pH OF LEACHATE FROM THE EXXON 27 SORBENT/ASH COMPACTS

Dwg. 2612C23

Sample	pH															
	Intermittent Shake, no. of 72 hr Intervals															1080 hr Cont's Shake
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
I 1C																8.5
I 1D	10.3	10.8	10.9	10.7	10.6	10.4	10.2	10.1	9.9	9.8	9.1	9.6	9.9	9.9	10.0	
I 2C																7.7
I 2D	10.2	11.0	11.0	10.9	10.7	10.6	10.2	10.2	9.7	9.6	9.5	9.2	8.9	8.7	8.6	
I 3C																7.9
I 3D	10.2	11.0	10.8	10.9	10.5	11.5	9.5	9.4	9.1	9.0	8.8	8.8	8.9	8.5	8.5	
I 4C' (Crushed)	11.3	11.3	11.1	11.1	10.9	10.9	10.7	10.7	10.7	10.7	10.6	10.4	10.3	10.1	10.1	
I 4D'	11.2	10.7	10.7	10.7	10.7	10.4	10.3	10.2	9.9	9.7	9.9	9.8	9.6	9.4	9.4	
II 1C																8.4
II 1D	11.5	11.4	11.5	11.2	10.9	10.9	11.0	11.4	10.9	10.9	10.9	10.6	10.5	10.2	9.5	
II 3C																8.7
II 3D	12.1	11.7	11.4	11.4	11.4	10.5	10.5	10.8	10.5	10.5	10.4	10.2	9.9	9.8	9.5	
II 3E																9.1
II 3F	12.0	11.7	11.6	11.4	10.9	10.5	10.6	10.8	10.4	10.2	10.3	10.2	9.9	9.8	9.7	
II 4C																8.3
II 4D	11.4	11.4	11.2	11.1	11.1	11.1	11.0	10.9	10.8	10.7	9.9	10.3	10.2	9.4	9.2	
II 4C'	12.2	11.8	11.6	11.7	11.5	11.5	11.2	10.5	10.7	10.7	10.7	9.8	9.8	10.2	10.2	
II 4D'	11.9	11.5	11.5	11.3	11.1	11.1	11.0	10.7	10.6	10.5	10.2	10.0	10.0	9.7	9.1	
III 2C																8.3
III 2D	11.9	11.5	11.5	11.2	10.6	11.0	10.9	10.9	10.9	10.0	10.0	10.3	9.8	9.8	9.3	
Unprocessed Exxon 19.6 Bed	12.3	12.1	12.2	12.1	12.2	12.2	11.9	11.7	11.6	11.4	11.1	10.6	10.4	10.2	10.3	
Unprocessed Exxon 19.6 Fly Ash	11.9	10.5	10.4	10.1	9.7	9.6	9.8	10.1	10.4	10.1	10.2	9.9	9.9	9.7	9.6	
Unproc. Exxon 27 Sorbent/Ash Mixture (80/20)	12.3	12.0	11.4	11.1	10.4	10.3	10.3	10.6	10.7	10.7	10.8	10.4	10.3	9.9	9.8	
Gypsum	7.7	7.6	7.8	7.6	7.6	7.6	7.5	7.3	7.4	7.9	7.6	7.4	7.5	7.5	7.3	

Table 29

Dwg. 2612C22

CALCIUM CONCENTRATION OF LEACHATE FROM THE EXXON 27 SORBENT/ASH COMPACTS

Sample	Calcium, mg/l															
	Intermittent Shake, no. of 72-hr Intervals															1080 hr Cont's Shake
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
I 1C																576
I 1D	572	544	544	400	344	320	248	224	296	208	212	136	168	164	168	
I 2C																552
I 2D	552	456	376	316	304	248	240	240	200	200	208	200	196	176	176	
I 3C																596
I 3D	548	520	432	336	360	344	296	288	256	248	224	224	192	184	176	
I 4C' (Crushed)	648	628	604	568	536	512	504	440	428	416	412	392	372	384	400	
I 4D'	604	432	352	328	280	264	268	240	280	248	240	240	216	232	256	
II 1C																560
II 1D	640	360	384	258	272	184	224	212	208	256	248	208	208	184	160	
II 3C																560
II 3D	896	584	388	328	376	296	240	220	184	176	168	152	148	136	144	
II 3E																576
II 3F	868	664	608	464	448	396	356	328	296	276	268	256	260	236	240	
II 4C																544
II 4D	600	544	3.6	300	200	204	264	160	152	152	180	152	200	176	168	
II 4C' (Crushed)	1224	832	720	680	632	596	548	488	508	448	440	416	420	416	404	
II 4D'	744	536	336	260	204	200	168	168	168	156	152	180	144	128	104	
III 2C																556
III 2D	776	408	328	260	260	232	160	188	208	184	204	168	200	192	160	
Unprocessed Exxon 19.6 Bed	1184	1336	1168	1232	1232	968	1008	800	744	700	680	652	644	528	600	
Unprocessed Exxon 19.6 Fly Ash	736	568	548	512	472	480	424	400	292	356	320	296	272	172	200	
Unproc. Exxon 27 Sorbent/Ash Mixture (80/20)	1024	1168	712	696	672	680	680	672	632	656	648	620	632	528	588	
Gypsum	632	608	624	616	596	624	616	608	616	608	624	632	624	616	608	

Table 30

SULFATE CONCENTRATION OF LEACHATE FROM THE EXXON 27 SORBENT/ASH COMPACTS

Dwg. 2612C21

Sample	Sulfate, mg/l															
	Intermittent Shake, no. of 72 hr Intervals															1080 hr Cont's Shake
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
I 1C																1692
I 1D	1600	1260	1071	903	885	704	555	515	690	400	850	418	530	575	503	
I 2C																1410
I 2D	1493	1105	840	683	710	641	565	555	418	489	503	488	448	408	418	
I 3C																1445
I 3D	1325	1175	876	737	720	665	627	633	549	487	530	503	455	425	382	
I 4C' (Crushed)	1353	1273	1260	1105	1225	1020	1083	991	885	950	885	830	777	840	858	
I 4D'	1236	893	745	632	710	611	632	620	650	632	590	530	440	548	522	
II 1C																1366
II 1D	983	543	682	420	611	403	543	487	470	543	536	674	502	522	395	
II 3C																1260
II 3D	1000	903	633	575	704	633	530	502	414	358	363	334	334	316	358	
II 3E																1475
II 3F	1040	1150	1060	932	894	813	751	650	620	536	575	543	555	650	603	
II 4C																1548
II 4D	1083	1128	543	509	488	438	555	440	368	343	457	348	466	406	439	
II 4C' (Crushed)	1212	1071	1225	1236	1645	1127	1116	950	1093	962	982	960	922	830	850	
II 4D'	1175	703	575	611	425	382	376	370	337	382	410	477	324	270	240	
III 2C																1565
III 2D	1163	751	620	503	620	575	399	529	439	399	466	399	466	414	363	
Unprocessed Exxon 19.6 Bed	1410	1247	1427	1187	1492	1272	1225	1690	1667	1622	1366	1260	1410	1010	1175	
Unprocessed Exxon 19.6 Fly Ash	1260	1083	1150	940	1127	893	950	950	730	830	565	633	530	355	438	
Unproc. Exxon 27 Sorbent/Ash Mixture (80/20)	1460	1352	1380	1285	1445	1175	1690	1737	1565	1582	1247	1175	1325	1010	1236	
Gypsum	1285	1187	1380	1285	1162	1000	1582	1475	1475	1547	1272	1272	1225	1352	1366	

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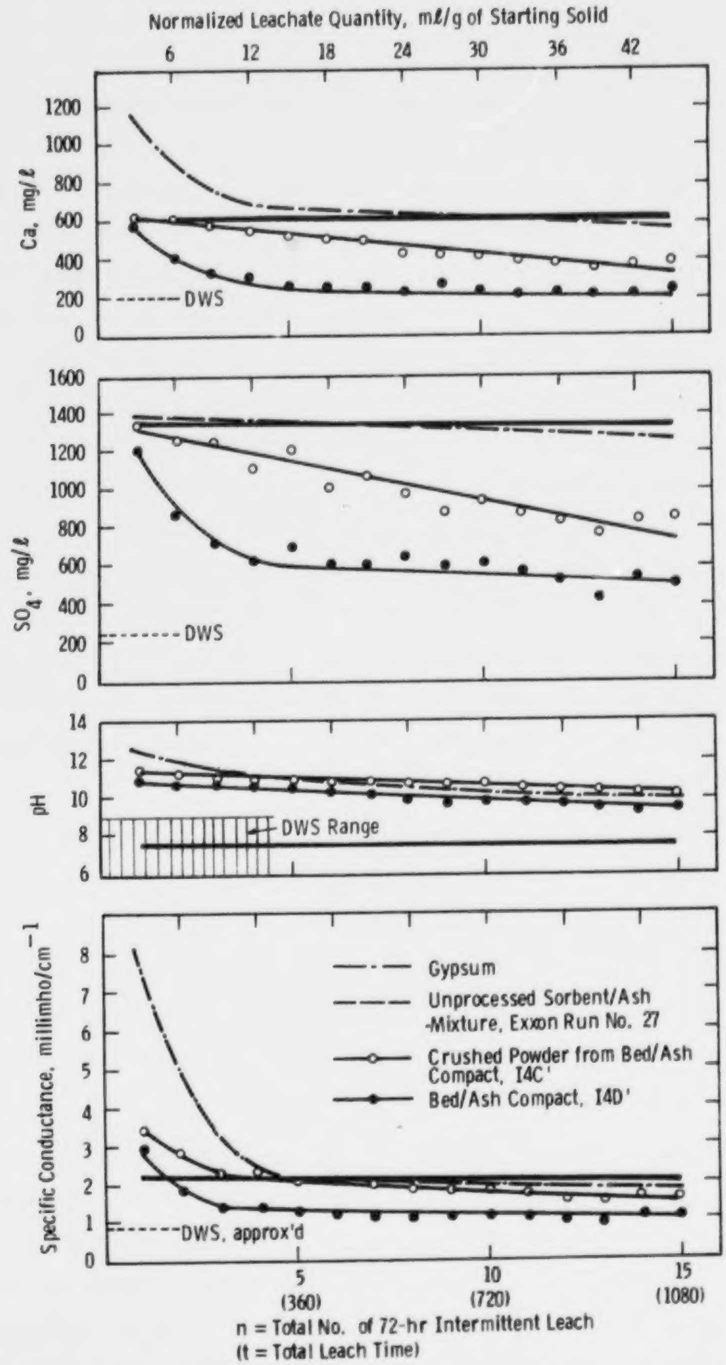


Figure 11 - Comparison of Leachate Characteristics of Processed Exxon 27 Sorbent/Ash Compact, Crushed Powder from Such Compact, Unprocessed Sorbent/Ash Mixture, and Natural Gypsum

trends. We note that the compact as cast and cured produced a leachate of better quality, i.e., lower calcium, SO_4, specific conductance, and pH, than that induced from the crushed compact in powder form, which in turn gave better leachate quality than did the unprocessed sorbent/ash mixture from the same FBC run. These findings are extremely important. The fact that the leachate of the crushed, fixed material was worse than that of the uncrushed compact indicates that the decreased surface area in the fixed (compact) FBC residue favorably affects the resultant leaching property, and suggests that increased leachability might result from fissuring a disposal pile of fixed FBC material. A mixture of unprocessed spent bed/carry-over had higher leachate concentrations, however, than did a crushed, fixed cube, indicating that processing has a favorable effect that will not be entirely eliminated by crushing or fissuring. Nevertheless, despite fixation/processing according to the procedures tested in Section 8, the initial leachate calcium, SO_4, and TDS are still above DWS. Comparison of leaching results from processed and unprocessed residues is presented in Section 8.

Figure 12, which one can extrapolate to long-term leachability, again indicates that gypsum leached constantly, independently of the total leach time and the volume of leachate passing through the sample. The leachates from the sorbent/ash compact, the crushed compact powder, and the unprocessed sorbent/ash mixture improved with time and total volume and, therefore, are much less contaminating with long-term leachability of $CaSO_4$ than is the natural gypsum.

Table 31 shows leachate characteristics of processed FBC residue as a function of leaching cycle from a series of ten 72-hr intermittent shake tests. The TOC was low throughout the tests. Figures 11 and 12, and Tables 27 through 30 show improvement of major species and pH. Table 31 illustrates a trend of decreasing trace element concentrations (e.g., Al, B, Ca, Cu, Mo, Si) in leachates as a function of repeated shake cycles. These concentrations are extremely low because the trace element concentrations in the initial leachate (first 72-hr shake) are below the DWS.

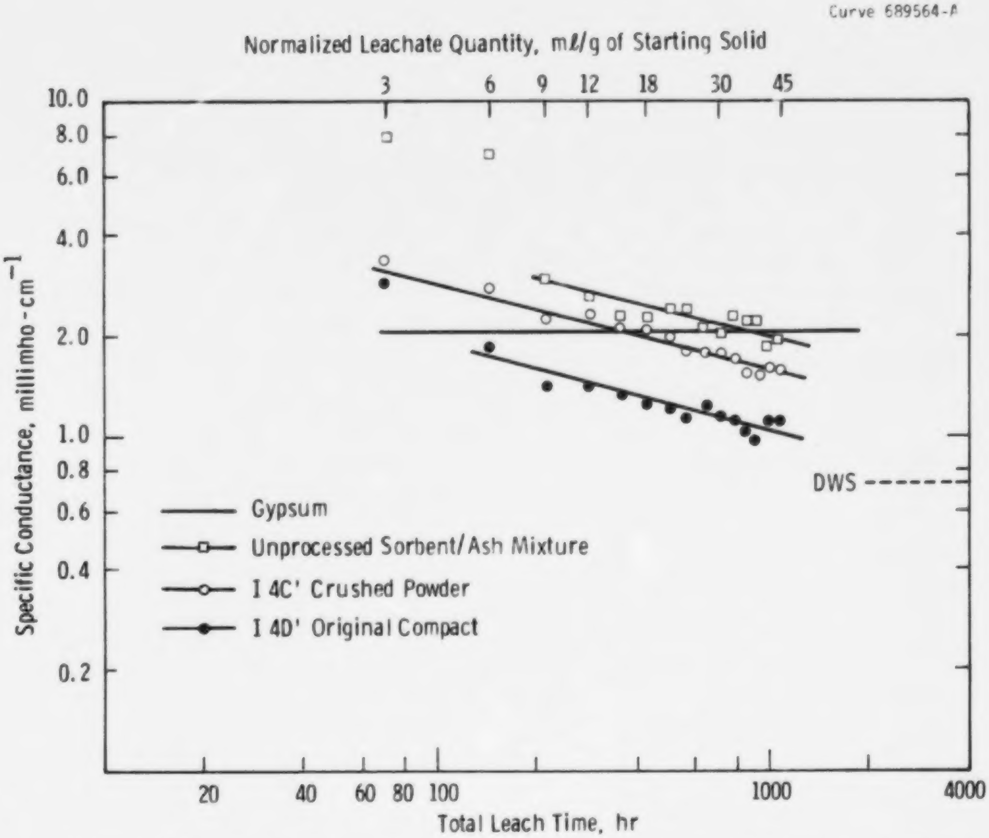


Figure 12 - Comparison of Specific Conductance of Leachates from Exxon 27 Sorbent/Ash Compact, Crushed Compact, Unprocessed Exxon 27 Sorbent/Ash Mixture, and Gypsum

Activity tests showed no heat release from these compacts on contact with water, as one would expect, since the casting involved a wet processing step in which CaO would have been hydrated.

Finally, results presented here clearly indicate that the sorbent/ash compacting process improves the leaching property and reduces the potential negative environmental impact of leachate contamination.

Leaching Medium Effect on Leachate

The leaching property of FBC residue was investigated as a function of leaching medium. Three media with varying pH levels were investigated. First, deionized water was used in the majority of the leaching tests (except where specified otherwise). Second, studies using CO_2-saturated

Dwg. 1709B90

Table 31

LEACHATE CHARACTERISTICS OF PROCESSED FBC RESIDUE AS A FUNCTION OF LEACHING CYCLE

(Ten 72-hr Intermittent Shake Tests of Compact II4D Prepared by Sorbent/Ash Blending Using Exxon 27 Solid)

Substance	Leachate of Processed FBC Compact, mg/ℓ [a]						DWS,[b] mg/ℓ
	1	2	3	5	7	9	
Al	0.3	0.3	0.3	0.2	0.1	0.1	
Ag	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.05
As	< 0.1	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.05
B	0.1	0.5	0.2	0.01	0.1	0.005	
Ba	< 1	< 1	< 1	< 1	< 1	< 1	1.0
Be	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	
Bi	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Ca	▨ 640	▨ 360	▨ 384	▨ 272	▨ 224	▨ 208	200
Cd	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01
Co	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	
Cr	< 0.03	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.05
Cu	0.01	0.01	0.01	0.005	0.005	< 0.005	1.0
Fe	0.01	0.02	0.02	0.005	< 0.005	< 0.005	0.3
Hg	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.002
Mg	< 10	19.2	< 10	< 5	14.4	< 10	150
Mn	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.05
Mo	0.03	0.02	0.01	0.003	0.003	< 0.003	
Ni	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	< 0.1	2.0
Pb	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	0.05
Sb	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	
Se	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.01
Si	> 30	> 20	> 20	> 10	> 10	> 10	
Sn	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	< 0.03	1.0
Ti	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
V	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	
Zn	< 1	< 1	< 1	< 1	< 1	< 1	5.0
Zr	< 1	< 1	< 1	< 1	< 1	< 1	
SO_4	▨ 983	▨ 543	▨ 682	▨ 611	▨ 543	▨ 470	250
TOC	< 10	< 10	< 10	< 10	< 10	< 10	
pH	▨ 11.53	▨ 11.42	▨ 11.54	▨ 10.85	▨ 10.97	▨ 10.94	6.5 to 9.2
SC, μmho/cm	▨ 2,740	▨ 1,750	▨ 1,810	▨ 1,250	▨ 1,200	▨ 1,080	~ 750

[a] Number of 72-hr intervals

[b] DWS - NIPDWR, USPHS, and WHO drinking water standards

▨ exceeds DWS

deionized water (pH = 4) were conducted to simulate surface water leaching where dissolved CO_2 might be high. The preliminary results with MERC residue discussed previously indicated that the effect of leaching with CO_2-saturated deionized water was not pronounced, probably because of the high alkaline content in the FBC residues. Third, leaching tests were also conducted using a sodium acetate/acetic acid buffer with a pH = 4.5 and a specific conductance of 3.3 millimho/cm, as suggested by the proposed ASTM test,[28] and as being considered by EPA under RCRA, to simulate an inhomogeneous disposal site where codisposal of municipal and industrial wastes often results in acidic leaching conditions. Results from Exxon 67 fines were discussed previously.

Several residues, in addition to that of Exxon 67, were tested using the buffered medium prepared by dissolving 4.9 g of glacial acetic acid and 3.7 g of sodium acetate in 1 ℓ of deionized water. The resultant buffer solution has a pH = 4.5 ± 0.1 and a specific conductance of 3.3 millimho/cm. The 200-hr continuous shake tests using the acidic buffer medium were carried out in the preliminary study presented here. The final leachate pH is dictated by the solid residue, since no additional acid was added to the original solid/acetate medium mixture.

Table 32 compares leachate characteristics of a variety of FBC residues (spent limestone and dolomite) and natural gypsum, using deionized water and a sodium acetate/acetic acid buffer solution as the leaching media. The samples listed in Table 32 are described in Table 8. Preliminary comparisons of the results indicate the following effects:

- The pH of the leachate resulting from the highly alkaline residue, using an acidic leaching medium, was decreased only slightly in comparison with deionized water. The one major exception was Exxon 67 fines, whose pH of 8 with deionized water fell to 4.7 with the buffer. This result is not surprising, since the Exxon 67 fines are not as strongly alkaline as the other residues.

Table 32

Dwg. 1702B01

COMPARISON OF LEACHATE CHARACTERISTICS
WITH WATER AND ACETATE LEACHING MEDIA
(200-hr Continuous Shake Tests)

Sample	Sorbent Type	Leach Medium	pH	Specific Conductance, millimho/cm	Ca, mg/ℓ	Mg, mg/ℓ	SO_4, mg/ℓ
Battelle Bed	Limestone	Dionized H_2O	12.1	8.6	1280	< 20	1083
Battelle Bed	Limestone	Acetate buffer	12.1	14.4	3040	< 20	812
Battelle Carry-over	Limestone	Dionized H_2O	12.0	8.4	1072	< 20	1150
Battelle Carry-over	Limestone	Acetate buffer	12.0	13.0	2640	< 20	982
B & W No. 19 Bed	Limestone	Dionized H_2O	12.2	9.24	1392	< 20	1200
B & W No. 19 Bed	Limestone	Acetate buffer	12.1	14.6	3064	24	1030
B & W No. 19 Carry-over	Limestone	Dionized H_2O	11.9	6.47	1184	< 20	1248
B & W No. 19 Carry-over	Limestone	Acetate buffer	11.4	8.7	1832	38	200
Exxon 43.2/43.3 Bed	Dolomite	Dionized H_2O	12.2	8.43	1304	< 20	1273
Exxon 43.2/43.3 Bed	Dolomite	Acetate buffer	12.1	13.9	2848	53	1339
Exxon 43.3 Carry-over	Dolomite	Dionized H_2O	11.3	2.99	672	< 20	1285
Exxon 43.3 Carry-over	Dolomite	Acetate buffer	9.2	9.0	1440	581	1763
ANL C2/C3 Bed	Dolomite	Dionized H_2O	11.9	3.98	960	< 20	1830
ANL C2/C3 Bed	Dolomite	Acetate buffer	10.0	9.0	1844	384	1188
Exxon 67 Carry-over, Fines < 15 μm	Dolomite	Dionized H_2O	8.0	9.16	488	1672	6975
Exxon 67 Carry-over, Fines < 15 μm	Dolomite	Acetate buffer	4.7	13.0	536	2016	7575
Gypsum	–	Dionized H_2O	7.4	2.15	615	< 20	1470
Gypsum	–	Acetate buffer	4.6	5.75	976	48	1445
Sodium Acetate/ Acetic Acid Buffer	–	–	4.5	3.31	–	–	–

- Leachate calcium was increased using a sodium acetate/acetic acid medium. This result is to be expected, also, since the low pH of the medium may be expected to cause additional quantities of the alkaline residue to dissolve in order to raise the leachate pH.
- Magnesium that was found to be insoluble in deionized water from spent dolomite sorbent was highly leachable in the acetate leaching medium. Again, this is due to the solubility of the alkaline residue in the acidic medium.
- The effect on leachability of SO_4 was not clear.
- Acidic acetate leaching resulted in increased specific conductance and TDS, because of the higher ionic strength and lower pH of the leaching medium. This effect was much more pronounced with FBC residues than with natural gypsum.
- Effects on trace elements were discussed earlier with regard to acid leaching of Exxon 67 fines. The concentrations of some trace metals in the leachate increased with the acidic medium, some decreased. Westinghouse is currently conducting further studies under the continuing contract to EPA.

Measurement of Total Dissolved Solids

The TDS in a leachate is a good index of leachate quality. Total dissolved solid, which can be determined by the time-consuming evaporating procedure, can also be estimated by multiplying the easily measured specific conductance by an empirical factor. This factor may vary, depending on the soluble components in the particular aqueous system and the temperature of measurement. We have selected a constant temperature, 25°C, for the latter throughout our leaching studies. This section summarizes our effort in determining the multiplying factor empirically for the FBC leachates.

Initially five samples -- Exxon 43.2/43.3 bed, Exxon 43.3/carry-over (ash), ANL C2/C3 bed, B&W 19 bed and carry-over (ash) -- were selected for this investigation to represent a broad spectrum of the FBC spent materials: limestone/dolomite, PFBC/AFBC, bed/carry-over (ash). Leachate was induced by a 48-hr shake procedure. A portion of the original leachate from each sample was diluted to provide solutions of 1/2, 1/4, and 1/8 fractions of the original concentrations. Specific conductance, pH, and TDS were determined for all 20 leachate solutions.

The procedure for determining TDS described in Standard Method for Water and Wastewater[33] was used to obtain TDS at the evaporating temperature of 103°C. This was not the true TDS because the residue at 103°C contained physically occluded water, hydration and carbonation products ($Ca(OH)_2$, $CaSO_4 \cdot \frac{1}{2} H_2O$, $CaSO_4 \cdot 2 H_2O$, and $CaCO_3$), among other dissolved species. To determine the true TDS (i.e., the total weight of solid dissolved from the spent FBC material), the residue at 103°C was heated to 500°C to convert $Ca(OH)_2$, $CaSO_4 \cdot \frac{1}{2} H_2O$, and $CaSO_4 \cdot 2 H_2O$ to CaO and $CaSO_4$; and then to 900°C to convert $CaCO_3$ to CaO. Since the solubility of $CaCO_3$ is extremely low, we can safely assume that any $CaCO_3$ present in the dissolved and dried solids would have to be formed by carbonation of the dissolved CaO in the aqueous phase and not from the dissolution of the $CaCO_3$ present in the original FBC residue. Since previous TOC measurements indicated a low dissolved organic content, volatilization and decomposition of organic species would not be of concern when drying at higher temperatures. We used the TDS at 900°C in this work because it represented more closely the weight of the actual solid components (e.g., CaO and $CaSO_4$) dissolved from the spent FBC materials.

Results presented in Figure 13 show the relation between TDS and specific conductance. Close examination of the data revealed that the two groups of data, represented by the two straight lines, were dependent on the pH of the original leachate. A lower TDS specific conductance factor [(0.37 mg/ℓ)/(μmho/cm)] resulted from samples whose original leachates had a pH in the vicinity of 12, and a larger slope [(0.87 mg/ℓ)/(μmho/cm)] resulted from samples with a lower pH (9 to 11). The reasons are clear: spent materials in the former case were rich in CaO, resulting in a higher pH and in greater conductivity due to the presence of large numbers of highly mobile and conductive hydroxide ions in the solutions. On the other hand, spent materials that were high in $CaCO_3$ and SiO_2 had lower hydroxide concentrations in their leachate and, therefore, lower conductivity and pH.

To verify the postulated grouping, eight additional samples were investigated. In addition to the FBC samples, these samples included four spent bed residues from the chemically-active fluidized bed (CAFB) process. These CAFB samples consisted of large quantities of CaO and very little SiO_2, since they were residues from CAFB oil gasification runs where coal ash was not present. The results from the additional eight samples shown on Figure 14 confirmed the slopes measured on the original five materials. Table 33 summarizes the correlation between TDS and conductance for all the samples studied.

Similar conclusions can be drawn for the FBC and the CAFB data. For spent materials with large amounts of CaO present (e.g., AFBC bed and carry-over, and PFBC bed where significant CaO is present), leachates generally have a pH of ∿12, and a specific conductance of >7000 μmho/cm. A multiplying factor of 0.37 should be applied to approximate TDS from specific conductance in this case. On the other hand, a higher factor, 0.87, should be multiplied by the specific conductance to estimate the TDS in leachates of spent materials with more $CaCO_3$ and SiO_2 (e.g., PFBC carry-over and most PFBC bed material where $CaCO_3$ is the major species). These leachates generally have a lower pH (<11.5) and lower specific conductance (2000 to 4000 μmho/cm).

Note that the results presented here are empirical, based on typical FBC leachates. The TDS obtained in this manner are only approximated values. Note that a typical FBC leachate has a TDS of approximately 3000 mg/ℓ and the DWS for TDS is 500 mg/ℓ.

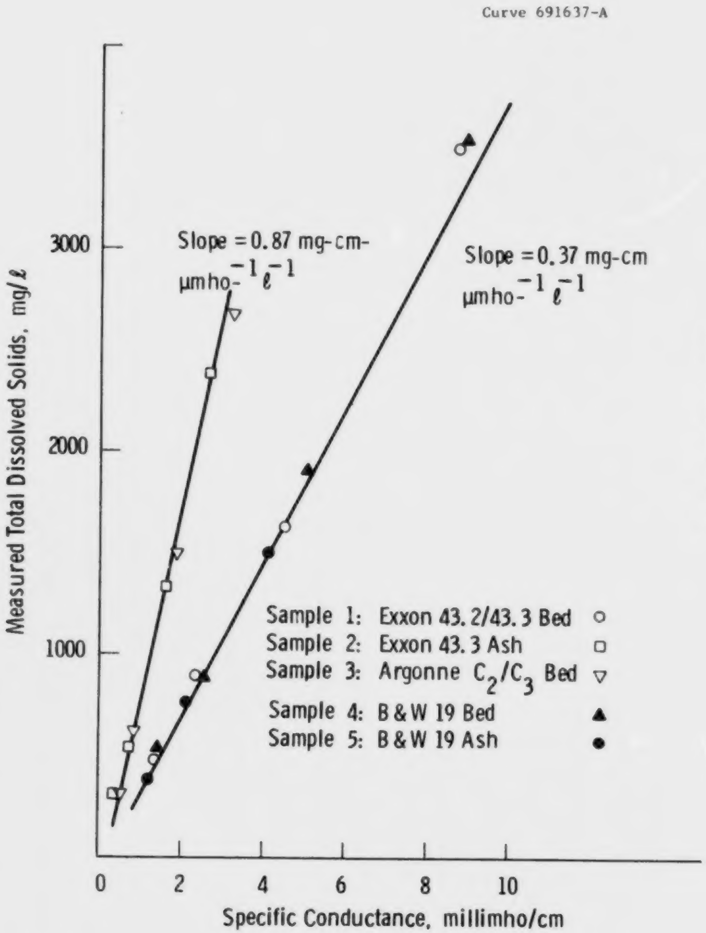


Figure 13 - Correlation between TDS and Specific Conductance in the FBC Leachate System

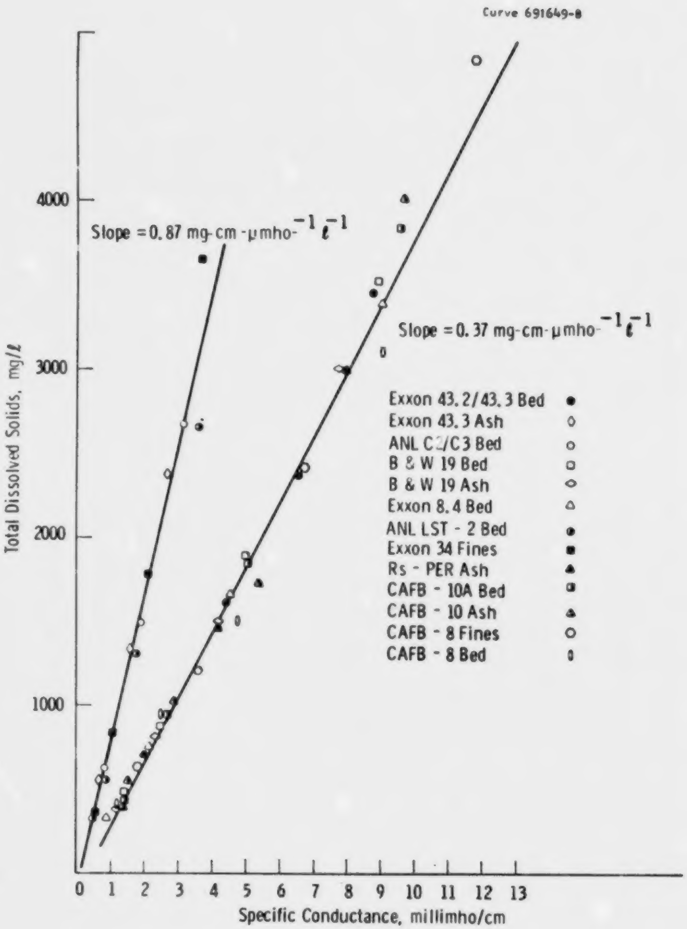


Figure 14 - Correlation between TDS and Specific Conductance in FBC and CAFB Leachates

Table 33

CORRELATION BETWEEN TDS AND SPECIFIC CONDUCTANCE

Sample	Description	pH	Sp. Cond., µmho/cm	Multiplying Factor, mg-cm-µmho^{-1}-ℓ$^{-1}$	Calculated TDS, mg/ℓ
ANL LST-2 Bed	PFBC bed, dolomite	11.3	3670	0.87	3193
ANL C2/C3 Bed	PFBC bed, dolomite	11.2	3240	0.87	2819
Exxon 43.3 Ash	PFBC ash, dolomite	9.1	3770	0.87	3280
Exxon 34 Fines	PFBC fines	11.0	2700	0.87	2349
Exxon 8.4 Bed	PFBC bed	11.8	8940	0.37	3309
Exxon 43.2/43.3 Bed	PFBC bed	12.0	8780	0.37	3249
B&W 19 Bed	AFBC bed	12.0	8980	0.37	3323
B&W 19 Ash	AFBC ash	12.0	7850	0.37	2905
RS-PER Ash	AFBC ash	11.8	8060	0.37	2980
CAFB-10A Bed	CAFB-gasifier bed	12.0	9610	0.37	3556
CAFB-10 Ash	CAFB-gasifier ash	12.0	9700	0.37	3589
CAFB-8 Bed	CAFB-regenerator bed	12.0	11900	0.37	4403
CAFB-8 Fines	CAFB-stack fines	12.0	11900	0.37	4403

Thermal Activity Tests

The activity of the residual lime in spent bed and carry-over material was determined by the lime's heat release property on contact with water, as the hydration reaction of CaO is extremely exothermic.[30] In an effort to select an appropriate activity test for the work reported here, we have reviewed the literature on lime reactivity and slaking rate tests. ASTM C110-76[31] provides a test for the slaking rate of quicklime (CaO). In this test 76 g of quicklime is added to 380 ml of distilled water in a modified Dewar flask covered with a rubber gasket fitted with a mechanical stirrer. The temperature is read with a thermometer at 30-second to 5-minute intervals, depending on the reactivity of the quicklime, until a constant temperature is reached. The slaking rate is determined by the following quantities: temperature rise at 30 seconds, total temperature rise, and active slaking time.

Murray[32] studied lime reactivity as a function of porosity and shrinkage characteristics during calcination and found that calcitic quicklime of low shrinkage and high porosity was highly reactive. He used a lime/water ratio of 1/7 by weight. Since preliminary slaking tests indicated a wide range in slaking rates, an empirical compromise point was selected as indicative of the rapidity of slaking. The temperature rise in five seconds was selected, and the reactivity coefficient was designated as ΔT_5. He readily acknowledges, however, that his test was based against the extremely reactive limes, in which slaking was actually completed in three to four seconds, so that a reading at five seconds made them appear to be slower than they actually were.

American Water Works's standard on lime for water treatment employs a lime slaking test with lime/water proportions of 100 g/400 ml, following the test procedure of ASTM-C110.

The temperature rise of a solid/water system containing free CaO is a function of solid/water ratio. In our experimental effort to establish a screening test for the residual activity in spent FBC solids produced under varying processing conditions, a solid to water proportion of 3 g to 20 ml (which is in the bulk range specified by the ASTM-C110 test and by Murray's work) was found empirically to provide much better repeatability than that from a higher solid/water ratio. A higher ratio would give greater temperature rise but would lack reproducibility, most likely because of local heating. The lower ratio was initially adopted as the screening test for heat-release property because of its speed, the small quantity of stone required, and the good reproducibility of results. A higher ratio (small quantity of water added to larger quantity of solid), however, was also used in some cases because it provides higher sensitivity and simulates rainfall onto the disposed solid.

Chromel-alumel thermocouples were used to monitor the temperature rise in the solid/water system with an Omega cold junction compensator and a millivolt recorder. The heat release tests were conducted on the actual spent sorbent, fly ash, and fines from the fluidized-bed combustion units. Calcined and uncalcined limestone and dolomite samples were also tested for comparison. Table 34 summarizes the maximum temperature rise when 3 g of solid were added to 20 ml of deionized water in a Dewar flask. The samples referenced are identified in Table 8.

Results showed that the spent solids from the once-through, pressurized FBC system gave off little heat spontaneously on contact with water. This finding is not surprising, since the $CaCO_3$ fraction of the spent solids from PFBC may be largely uncalcined because of the high CO_2 partial pressure that exists in PFBC units, unless the bed temperature is high enough to cause calcination.

In cases where there was residual CaO present in the PFBC samples, they might have been hydrated in air during storage, dead-burned during the process, or coated with impermeable $CaSO_4$ so that little spontaneous heat of hydration was detected. The only batch of the once-through PFBC spent materials that released detectable heat was the spent sorbent from Exxon 43.3. It had an average bed temperature of 940°C, which is high enough to calcine the $CaCO_3$ even at the elevated CO_2 partial pressures in PFBC. This sample showed a gradual temperature rise over 35 minutes

Table 34

HEAT RELEASE PROPERTY OF FBC WASTE

Dwg. 2619C51

Process	FBC Unit	Run	Source	Solid/Water	ΔT_{max}	Remark
PFBC, Once-thru	ANL	C2/C3	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	ANL	VAR-4	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	ANL	LST-1	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	ANL	LST-2	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	ANL	LST-3	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	ANL	LST-4	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	Exxon miniplant	8.4	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	Exxon miniplant	27	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	Exxon miniplant	19.6	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	Exxon miniplant	30.2	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	Exxon miniplant	43.2	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	Exxon miniplant	43.3	Bed	3 g/20 ml	1.4°C	Over 35 min Slow Rise
PFBC, Once-thru	Exxon miniplant	43.2/43.3	Bed	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	Exxon miniplant	30.4	Bed	3 g/20 ml	< 0.2°C	Sample obtained via RS; previously hydrated and dried by RS
PFBC, Once-thru	Exxon miniplant	19.6	Cyclone ash	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	Exxon miniplant	27	Cyclone ash	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	Exxon miniplant	26	Cyclone ash	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	Exxon miniplant	30.4	Cyclone ash	3 g/20 ml	< 0.2°C	Sample obtained via RS
PFBC, Once-thru	Exxon miniplant	43.5	Cyclone ash	3 g/20 ml	< 0.2°C	Sample obtained via RS
PFBC, Once-thru	Exxon miniplant	26	Fines	3 g/20 ml	< 0.2°C	
PFBC, Once-thru	Exxon miniplant	67	3rd cyclone fines < 15μm	3 g/20 ml	1°C	In 3 min
PFBC, Regenerative	ANL	REC-3	Comb. bed	3 g/20 ml	< 0.2°C	
PFBC, Regenerative	ANL	CCS-10	Reg' tor bed	3 g/20 ml	< 0.2°C	
PFBC, Regenerative	Exxon miniplant	45	Comb. bed	3 g/20 ml	0.5°C	Very slow rise over 1.5 hr
PFBC, Regenerative	Exxon miniplant	45	Reg. bed (granular)	3 g/20 ml	2°C	Over 2 hr
PFBC, Regenerative	Exxon miniplant	45	Reg. bed (agglomerated)	3 g/20 ml	< 0.2°C	
PFBC, Regenerative	Exxon miniplant	45	Cyclone ash	3 g/20 ml	< 0.2°C	
PFBC, Adiabatic	Combustion Power	P-403	Baghouse fines	3 g/20 ml	< 0.2°C	Old sample stored > 1 yr

Table 34 (Continued)

Dwg. 2619C52

Process	FBC Unit	Run	Source	Solid/Water	ΔT_{max}	Remark
AFBC, Once-thru	PER	Unidentified	Bed	3 g/20 ml	<0.2°C	Highly sulfated, from a storage pile of unknown history and age
AFBC, Once-thru	PER	Shakedown	Bed	3 g/20 ml	10.1°C	Sample via RS
AFBC, Once-thru	PER	Unidentified	Fly ash	3 g/20 ml	1.8°C	Sample via RS
AFBC, Once-thru	B & W	19	Bed	3 g/20 ml	11°C	
AFBC, Once-thru	B & W	19	Fly ash	3 g/20 ml	1.0°C	
AFBC, Once-thru	MERC	3/9/77	Bed	3 g/20 ml	7°C	In 30 min
AFBC, Once-thru	MERC	3/9/77	Cyclone ash	3 g/20 ml	0.8°C	
AFBC, Once-thru	MERC	3/9/77	Baghouse fines	3 g/20 ml	1.2°C	In 15 min
AFBC, Once-thru	Battelle	Erosion/ corr. run	Bed, 1000 hr	3 g/20 ml	< 0.2°C	In 1 hr
AFBC, Once-thru	Battelle	Erosion/ corr. run	Bed, 1500 hr	3 g/20 ml	3.5°C	In 10 min
AFBC, Once-thru	Battelle	Erosion/ corr. run	Cyclone ash 600 hr	3 g/20 ml	3°C	In 15 min
AFBC, Once-thru	Battelle	Erosion/ corr. run	Cyclone ash 1500 hr	3 g/20 ml	2.5°C	In 1 hr
Gypsum, Iowa 114				3 g/20 ml	< 0.2°C	Varies with types of limestone and calcination temperature and time
Limestone, 1359				3 g/20 ml	< 0.2°C	
Dolomite, Tymochtee				3 g/20 ml	< 0.2°C	
Calcined Limestone 1359, +35 −18Mesh				3 g/20 ml	> 55°C	

to reach a maximum of 1.4°C. These results seem to indicate that heat release may not be a problem for the once-through PFBC process. One must bear in mind, however, that the heat release property of spent sorbent is a function of the processing conditions; e.g., temperature, stone residence time, degree of sulfation, and degree of dead-burning.

We also observed moderate and slow temperature rise for the regenerative PFBC spent sorbent when contacting water. This rise is due to the presence of CaO formed during the one-step regeneration process.

All the spent solids from the AFBC system showed significant heat release characteristics, with the exception of an aged PER sample that had an unidentified process and storage history; its result, therefore, should be discarded. We judge that the heat release property of the spent sorbent from the AFBC process would probably require special care in handling and disposal.

The results presented in Table 34 also indicate that the spent bed material had much higher thermal activity than did the carry-over. This finding is easily understood in the light of the fact that the carry-over material generally contains more coal ash and less CaO, which is responsible for the heat release. Despite the fact that the AFBC bed material may cause concern because of its thermal activity, the rate and magnitude of heat it releases when contacting water is much less than the calcined limestone release, which represents the upper limit case (where neither sulfation nor high-temperature dead-burning of CaO nor contamination of coal ash takes place).

We also investigated the heat release property using higher solid/water ratios. Figure 15 compares the temperature rise as a function of solid/water ratio for an AFBC spent sorbent and a calcined limestone. A higher temperature rise and a faster response are observed when a smaller amount of water is added to a larger amount of solid, as is expected. Figure 16 shows the temperature rise profile when 4 ml water are added to 16 g of AFBC spent solid. A lower solid/water ratio was used for the calcined limestone because of the limestone's extremely

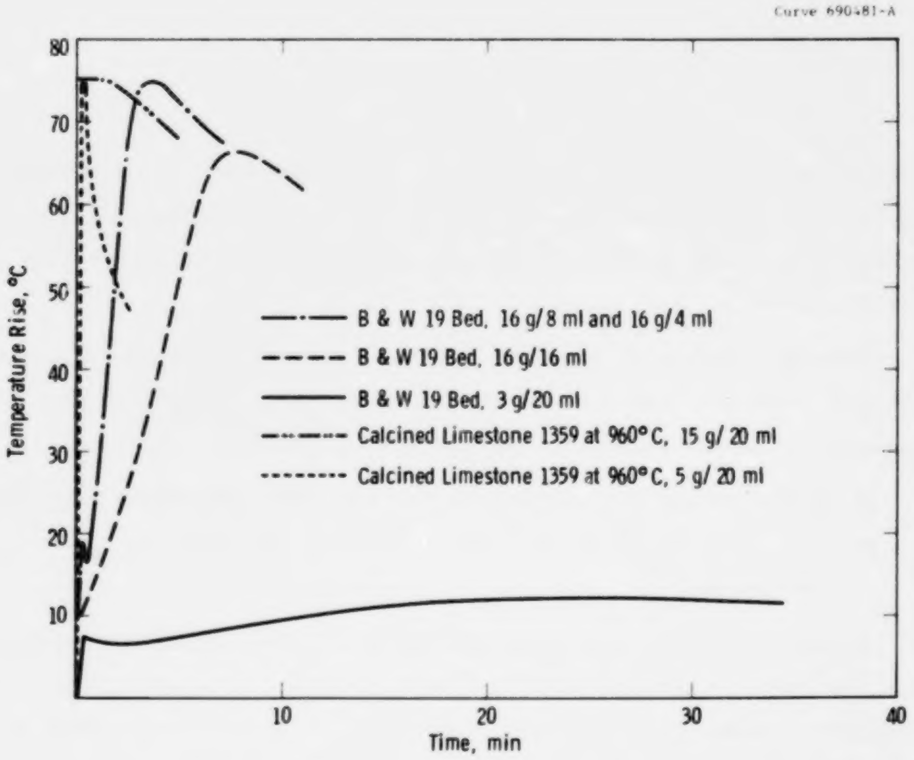


Figure 15 - Heat Release Property as a Function of Solid/Water Ratio

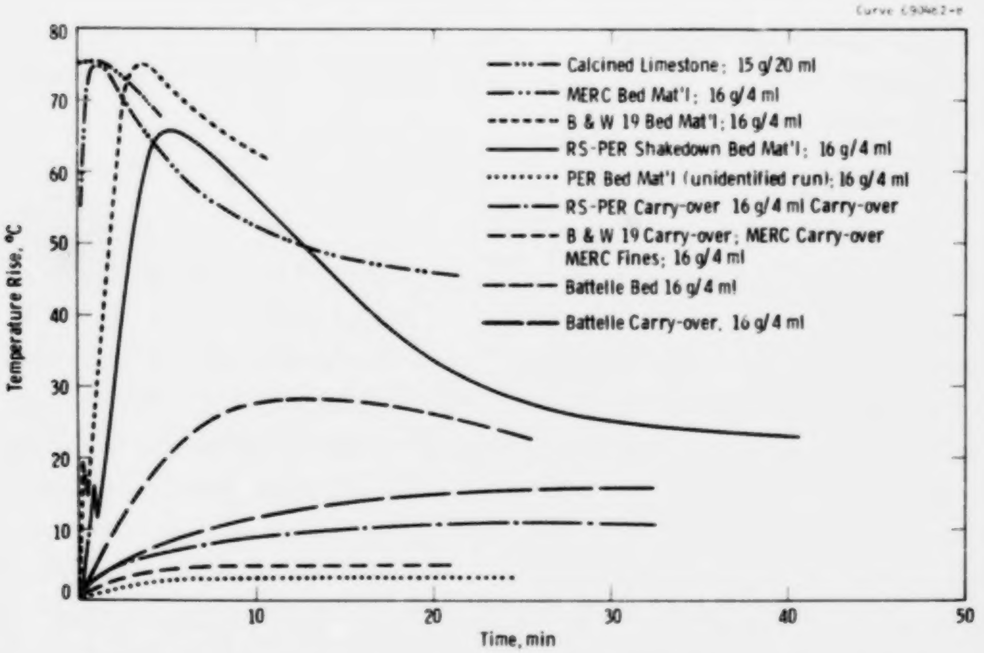


Figure 16 - Heat Release Property of Spent Bed and Carry-over from the Atmospheric FBC System

violent heat release characteristics. The same data are presented in Figure 17, which emphasizes the difference among the initial heat release characteristics of various solids by plotting the total time on a logarithmic scale.

Finally, Figure 18 compares the heat release property of spent bed material, fly ash, and fines from the AFBC, PFBC (once-through and regenerative), and adiabatic systems and illustrates that:

- AFBC residue has higher thermal activity than does PFBC residue
- Spent bed material has higher thermal activity than does spent carry-over.

Figure 18 shows once again the general trend indicated in Table 34, that the heat release property decreases in the following order: calcined limestone → AFBC bed → AFBC ash → PFBC bed, regenerative → PFBC bed, once-through → PFBC ash. Since P-403 ash that has been stored for over one year is the only material available from the Combustion Power adiabatic process and since the CaO content of this sample may have hydrated during the storage period due to moisture in the air, the heat release property of the adiabatic combustor system must be investigated further.

PERFORMANCE SUMMARY

Leaching property was investigated for over 30 samples of FBC residue, including spent limestone and dolomite sorbent and carry-over, from pilot-scale fluidized-bed combustors and regenerators of both the atmospheric and pressurized systems. Both the continuous and the intermittent shake tests were employed.[34] Figure 19 summarizes the results from the continuous shake test, showing the chemical characteristics of leachates from spent FBC bed (sorbent) and carry-over (ash) materials caused predominantly by the dissolution of the major species, CaO and $CaSO_4$. The results formed two broad bands each for calcium, SO_4, pH, and specific conductance in the FBC leachate. The average leachate from the FBC ash was better than that from the spent bed material because of the higher SiO_2 and lower CaO present in the fines. Leachate

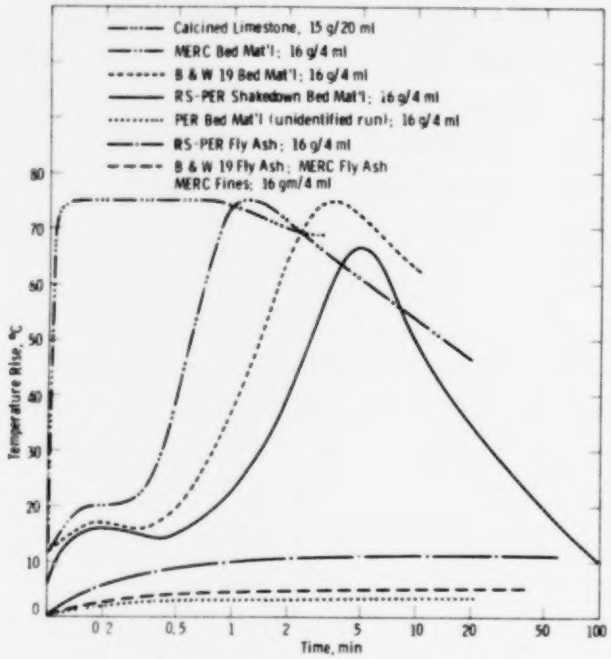


Figure 17 - Heat Release Property of Spent Sorbent and Fly Ash from the Atmospheric FBC System

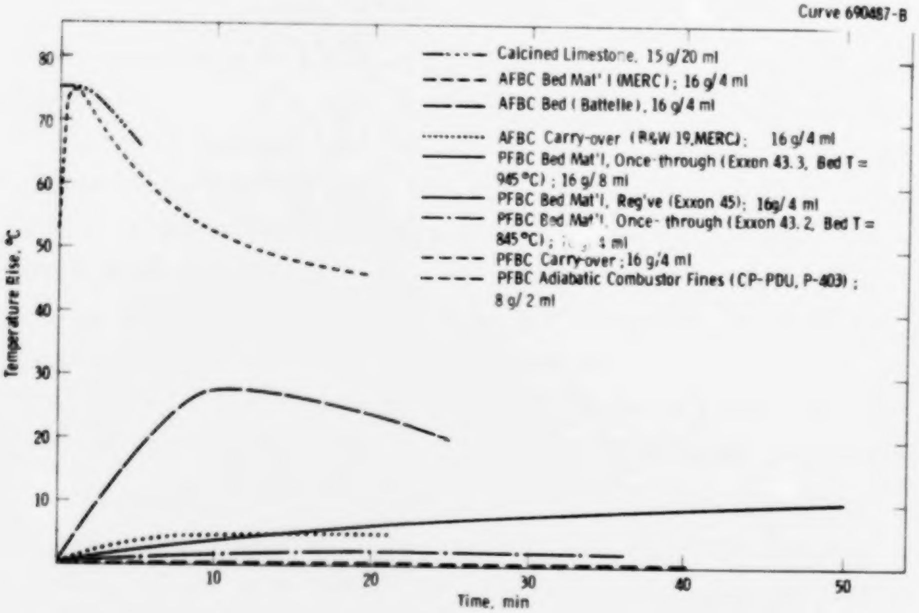


Figure 18 - Comparison of Heat Release Property of Spent Bed and Carry-over from the FBC Process of Different Processing Variations

from most of the FBC carry-over, except for its higher pH, was similar, to that from a natural gypsum. Leachate from spent bed material was generally of poorer quality than that from natural gypsum, except in the $SO_4^=$. In contrast with the constant leachability over time for the natural gypsum, the FBC leachate showed a slow but steady improvement with continuous leaching time (over 400 hours), most likely because of a reaction with CO_2 in air.

Figure 20 shows results from the 72-hour intermittent shake test, again showing two bands of data, with carry-over leachate superior to the spent bed leachate. The average leachate from the FBC carry-over also improved faster with time, as well as with the total volume of leachate passing through the residue, than did the spent bed material. Magnesium was not presented in these figures because it was generally found to be insoluble from the FBC residue, including spent dolomite sorbent, with only one exception (Exxon 67 third-cyclone fines, discussed earlier). Sulfide is below the detectable level in leachate from once-through residue but should be investigated further for the regenerative FBC system.

Total organic carbon was found to be as low (<10 ppm) as that in a natural gypsum leachate for all FBC residues (below or near the detection level) except for one carry-over (30 ppm for MERC bag-filter fines). Leachability of the trace metal ions was low for all the spent FBC material, so that all except two batches of carry-over collected after the second cyclone (MERC bag-filter fines and Exxon 67 third-cyclone fines) met the DWS for trace elements for which a DWS exists. The low metal concentration in FBC leachates is understandable since the leachates are highly alkaline, and the solubilities of the practically insoluble metal hydroxides and carbonates control the trace metal ion concentrations.

Leaching property is a function of the pH of the leaching medium and the resultant leachate. Initial results from sodium acetate/acetic acid leaching (pH $\sim$4.5) were noticeably different from the leachate

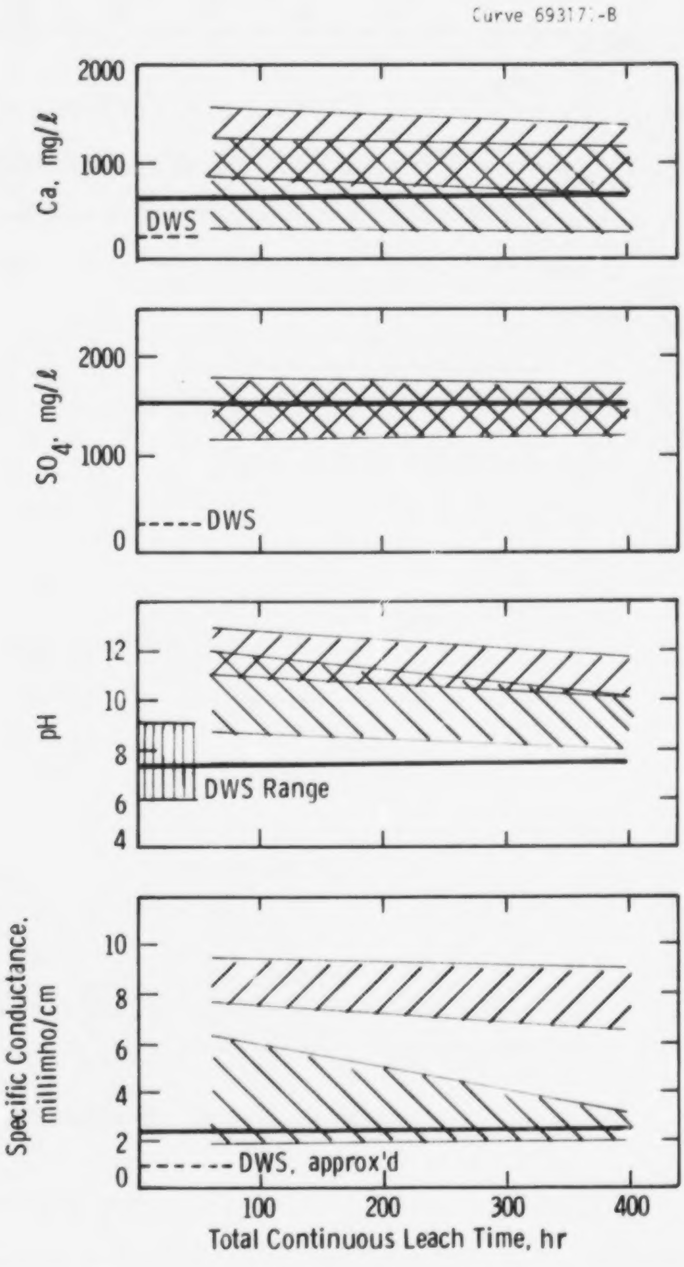


Figure 19 - Leachate Characteristics as a Function of Continuous Leaching
▨ Bed Material, ▧ Carry-over, —— Gypsum

Curve 693170-B

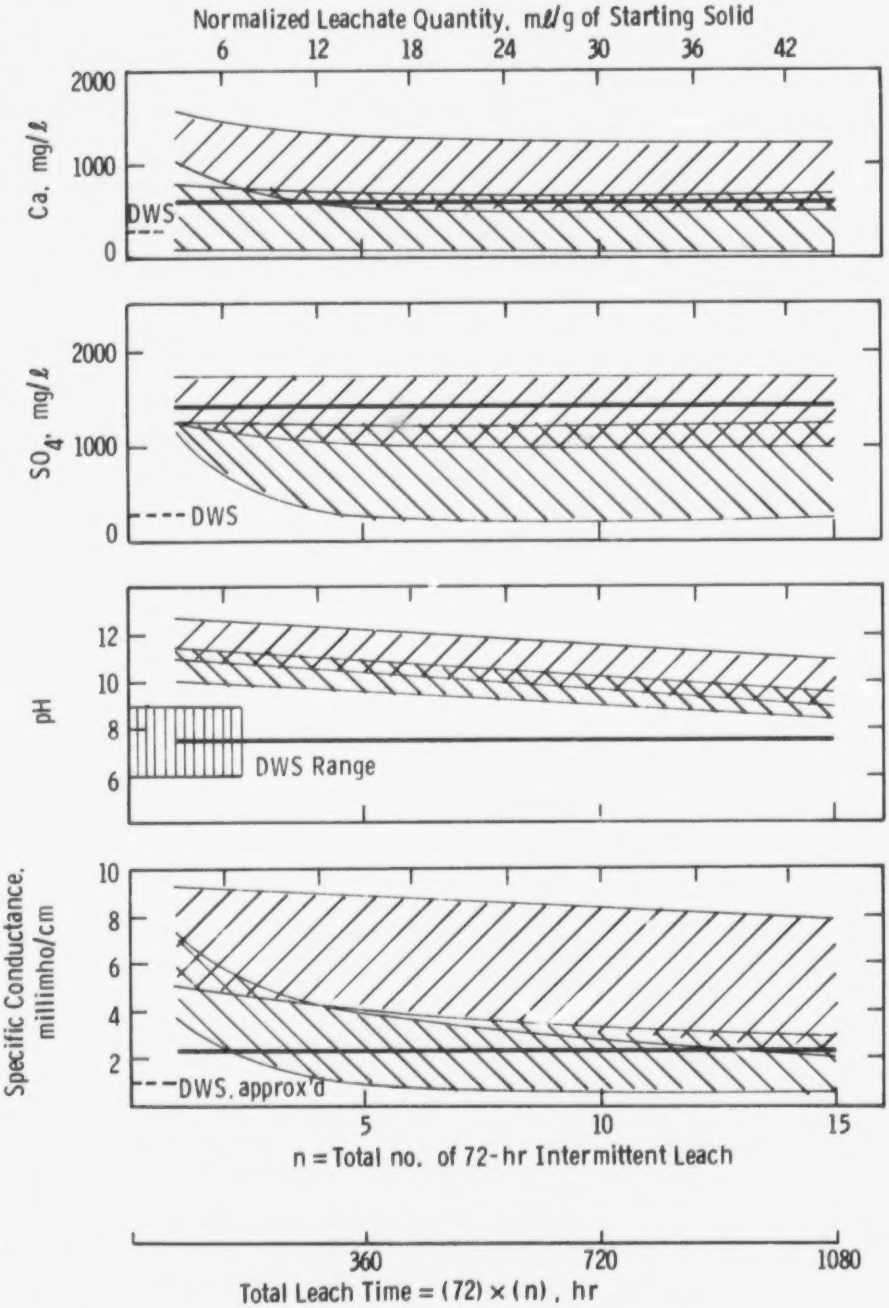


Figure 20 - Leachate Characteristics as a Function of Intermittent Leaching. ▨ Bed Material, ▧ Carry-over, —— Gypsum

induced with deionized water in both major species and trace elements. Further investigation is required and is being carried out under our continuing contract with EPA to determine the effect of the pH of the leaching medium on the leaching property of FBC residue.

Lacking EPA's criteria on heat release property from solid waste disposal, we evaluated the environmental acceptability of the FBC spent solids on the basis of their potential residual heat release activity on a relative scale. The results to date indicate that:

- Heat release would not be a problem for the once-through PFBC process, if the bed temperature is low enough, because of the large amount of $CaCO_3$ present.
- The heat release property of the spent sorbent from the AFBC process would probably cause environmental, occupational, and handling concerns because of the large quantity of CaO present.
- The spent bed material has a higher activity than do the carry-over fines from the same system.
- Spent sorbent from the regenerative system may contain CaO from the one-step regeneration reaction, and its heat release property depends on the composition of the spent sorbent.

Some spent sorbents, however, contained CaO but released very little heat when contacting water. In such cases the CaO must have been hydrated in air during storage, dead-burned during the process, or coated with impermeable $CaSO_4$ so that no temperature rise was detected.

We must emphasize that the preliminary results presented here are based on the limited number of available FBC residues investigated and that the heat release property of spent sorbent is a function of the FBC conditions - temperature, sorbent residence time, degree of sulfation, and degree of dead-burning.

Further processing of FBC residue by a sorbent/ash compacting process improves the leaching and heat release properties and reduces the potential environmental impact through leachate contamination.

Table 35

Dwg. 2612C01

PRELIMINARY INDICATIONS OF ENVIRONMENTAL IMPACT OF FBC SOLID WASTE DISPOSAL[a]

Sample	Process	Sorbent Type	Environmental Parameters								
			Heat Release(b,c) (spontaneous temp rise), 3 g/ 20 ml	Trace Metal	Total Dissolved Solids	Total(b) Organic Carbon	pH	Calcium	Sulfate	S =(b)	Mg
Bed Material	Pressurized FBC, once-through	Limestone	< 0.2°C		▩	< 10 ppm	▩	▩	▨		
Bed Material	Pressurized FBC, once-through	Dolomite	< 0.2°C		▨	< 10 ppm	▩	▨	▨		
Bed Material	Pressurized FBC, regenerative	Dolomite/limestone	0-3 °C		▩	< 10 ppm	▩	▩	▨	▩	
Bed Material	Atmospheric FBC, once-through	Limestone	5 to 15°C		▩	< 10 ppm	▩	▩	▨		
Carry-over Material	Atmospheric FBC, once-through	Limestone	0-3°C	(d)	▩	< 30 (e) ppm	▩	▩	▨		
Carry-over Material	Pressurized FBC, once-through	Limestone/dolomite	< 0.2°C	(d)	▨	< 10 ppm	▩	▨	▨		(d)
Mixtures of Bed and Carry-over Material (unprocessed)	Pressurized FBC, once-through	Dolomite/limestone	< 0.2°C		▨	< 10 ppm	▩	▨	▨		
Processed Compacts from Bed Carry-over Mixtures	Pressurized FBC, once-through	Dolomite/limestone	< 0.2°C		▨	< 10 ppm	▩	▨	▨		
Gypsum	Natural		< 0.2°C		▨	< 10 ppm		▨	▨		

▩ Do not meet either the drinking water or gypsum leachate criteria.

▨ Pass gypsum leachate criteria but not drinking water standards.

☐ Pass both drinking water and gypsum leachate criteria.

(a) Based on data from currently available FBC residues

(b) No existing criteria

(c) Subjected to the specified procedures

(d) All except two carry-over fines pass drinking water standards

(e) All except one <10 ppm

Table 35 summarizes preliminary indications of the environmental impact of FBC solid waste disposal. Since we lacked definite disposal criteria, we compared leachate characteristics with DWS, and with leachate from natural gypsum, to put leachate quality into perspective.

7. CONVENTIONAL POWER PLANT RESIDUE ENVIRONMENTAL IMPACT TESTS

In order to provide another point of comparison, we repeated the tests described previously on FBC residue on samples of sludge from flue gas desulfurization (FGD) systems in conventional boilers.

FGD RESIDUE TEST RESULTS

After settling, a typical untreated FGD sludge using lime or limestone sorbent contains 30 to 70 percent solid matter. The major constituents of the solid are $CaSO_3 \cdot 1/2\ H_2O$, $CaSO_4 \cdot 2\ H_2O$, $CaCO_3$; coal ash that consists of SiO_2, Al_2O_3, Fe_2O_3; and trace elements. The exact composition varies, depending on many factors, including the type of coal, the type of scrubber system, and boiler and scrubber operating conditions.

Six samples of FGD sludge from pilot- and commercial-scale SO_2 scrubbing systems were tested during this investigation. These included: untreated, ponded, oxidized, and stabilized lime or limestone scrubber sludges. Table 36 summarizes the sample source, scrubber system, further treatment, and X-ray identification of the sludges. All sludge samples except one (the stabilized) were wet with supernatant liquors as received. The liquors were separated by vacuum filtration and chemically analyzed. The dewatered sludges were then dried ($\sim$95 to 105°C), and the sludge powders underwent the leaching tests described previously for FBC residues.

Figure 21 shows photomicrographs of three types of FGD residues investigated on the left (untreated, oxidized, and stabilized) and three sources of FBC residue on the right (bed, carry-over, and fines collected from the final particulate control device). Microscopic examination of the dried FGD sludges by SEM shown on the left half of Figure 21 reveals

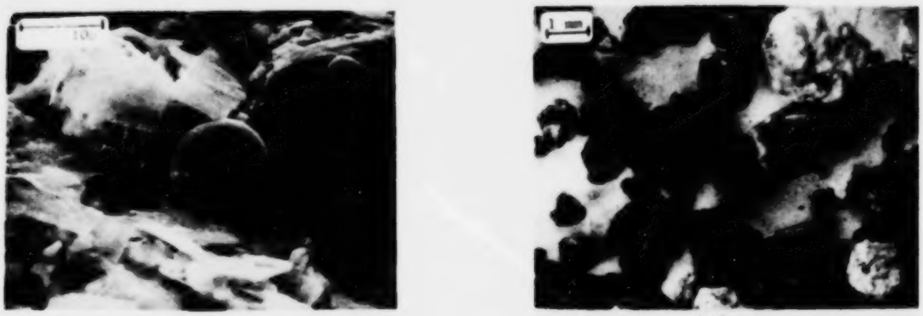
Table 36

SUMMARY OF FGD SLUDGE SAMPLES

Sample	Process Description	X-Ray Identification
Louisville Gas and Electric Company (LGE)[35]	Fresh, untreated, unponded; lime sludge with small amount of MgO added	Major: $CaSO_3 \cdot 1/2\ H_2O$ Low minor: (Fe,Mg) Al_2O_4 or (Mg,Fe) SiO_4 spinel
Columbus Southern Ohio Company (CSO)[36]	Untreated lime sludge; 98% fly ash removal	Major: $CaSO_3 \cdot 1/2\ H_2O$
Duquesne Light Company (DLC)[36]	Untreated lime sludge; containing ∿50% fly ash	Major: SiO_2 Minor: $CaSO_3 \cdot 1/2\ H_2O$ Low minor: Fe_2O_3
TVA Shawnee, Pond E[37,38]	Untreated, ponded limestone sludge bottled in pond liquor for 2.5 yr	Major: $CaSO_3 \cdot 1/2\ H_2O$ Major: $CaCO_3$ Trace: SiO_2
TVA Shawnee – Oxidized Sludge[37,39]	Lime sludge followed by forced air oxidation to gypsum	Major: $CaSO_4 \cdot 2\ H_2O$
Duquesne Light Company – Stabilized Sludge[36]	"Calcilox" stabilized lime sludge containing ∿50% fly ash; stabilized and ponded for 3 yr	Major: SiO_2, amorphous phase Minor: $CaCO_3$, $CaSO_3 \cdot 1/2\ H_2O$

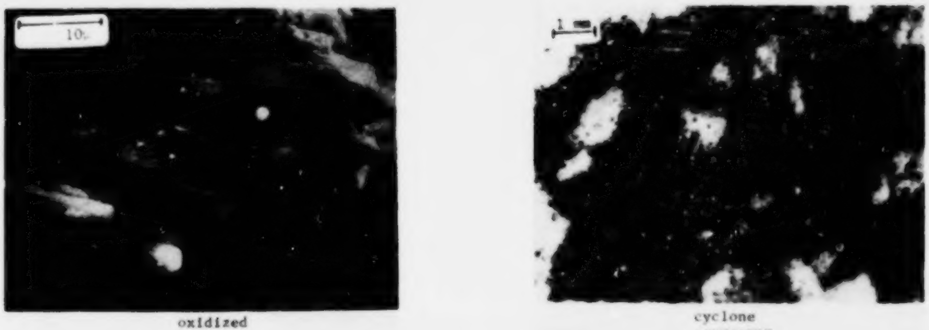
FGD Sludge (dried)

FBC Solid Waste



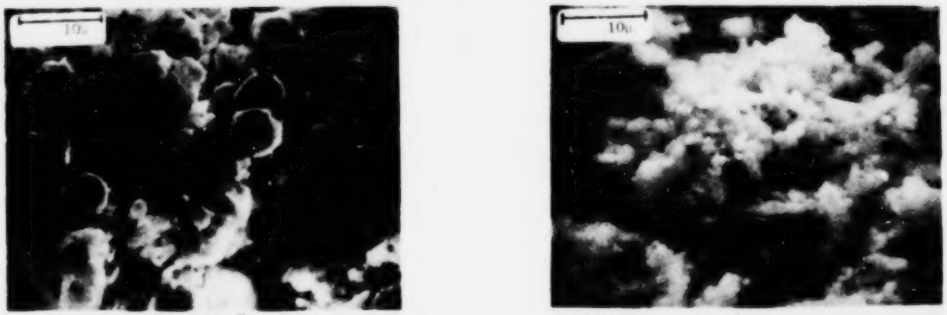
untreated

bed
material



oxidized

cyclone
carryover



"Calcilox"
stabilized

stack
carryover

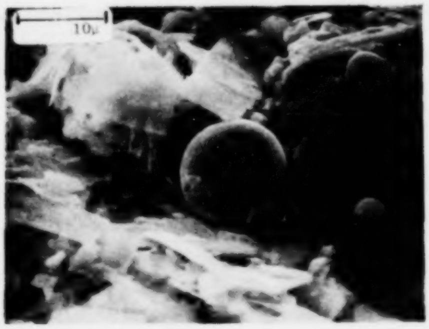
Figure 21 - Comparison of FBC and FGD Residue Photomicrographs

the difference in the physical characteristics among the three FGD samples. The unprocessed sludge exhibits the small platelet crystallites of $CaSO_3 \cdot 1/2\ H_2O$ that have been reported by the FGD investigators[35-38] to be responsible for the difficulties with dewatering and settling, as well as the thixotropic property of the untreated sludge. The ponded sludge often has mixtures of the flaky platelets and bulkier crystals that result from partial oxidation of sulfite to sulfate. On the other hand, the oxidized TVA sludge shows large crystals of gypsum ($CaSO_4 \cdot 2H_2O$). The potential environmental hazard (due to sulfite oxygen demand) has been reduced, and dewatering and settling difficulties are greatly improved. In fact, oxidation to gypsum has been recommended as one of the methods by which to stabilize FGD sludge.[39] Cenospheres from coal ash are also present in the sludge samples and may also cause settling problems in ponding. Photographs of the stabilized sludge shows a mixture of cenospheres and a fluffy mass that appears frequently to be clustered and to adhere to the cenospheres. The platelet crystallites are no longer evident. Dravo has reported that the compressive strength of the stabilized sludge increases as a function of curing (solid setting) time in a manner similar to concrete.[40]

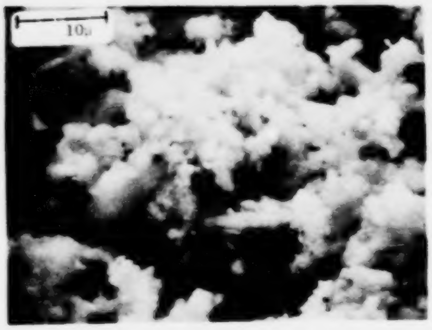
The right side of Figure 21 shows that the FBC residues are granular solids from the bed and much finer particles in the carry-over material. The absence of the cenospheres in FBC ash, including the fines collected in the third cyclone (note the different magnification in the third-cyclone photo because of its finer size), is in vivid contrast to the appearance of conventional coal ash. This difference is understandable, as FBC is operated at a much lower temperature than are the conventional boilers.

EDAX spectra (Figure 22) show that the platelet crystallites of the FGD solid are high in calcium and sulfur (presumably $CaSO_3 \cdot 1/2\ H_2O$), that the cenospheres are rich in silicon, aluminum, and iron (coal ash), and that the FBC stack carry-over consists of intimate mixtures of coal ash (produced under FBC conditions) and sorbent fines.

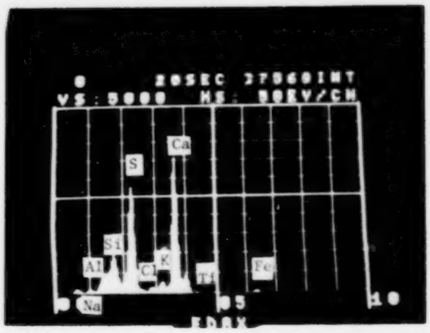
SEM and EDAX of FBC and FGD Ash



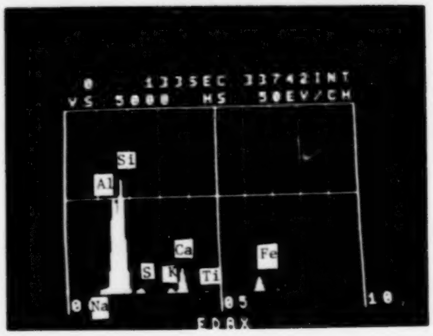
(c) FGD Sludge (TVA)



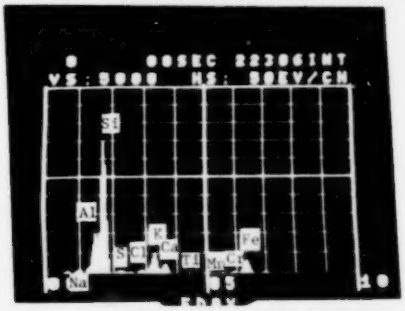
(a) FBC Ash (Exxon)



(d) FGD Sludge, Platelet



(b) FBC Ash, Area Scan



(e) FGD Sludge, Cenosphere

Figure 22 - SEM and EDAX of FBC and FGD Ash

Leaching properties were investigated using both the continuous and the intermittent shake methods described in the previous section. These samples resulted from processes using different coals/sorbents; absolute comparison of one process versus another, therefore, may not be possible, although one would hope that the general trends indicated would be meaningful.

Figure 23 shows leachate characteristics of the dried sludge as a function of continuous leaching time. One can see that the leachate from the stabilized FGD sludge is very similar to leachate from gypsum. On the average the untreated sludge leachate has higher levels of calcium, magnesium, SO_4, pH, and TDS. As in the case of FBC residue, the leachate of FGD residue also exceeded the DWS in calcium, SO_4, and TDS. Unlike the FBC leachate, however, the pH of FGD leachate fell within the DWS range.

Figure 24 shows the specific conductance in the leachate from the intermittent shake test. The better initial leachate quality is again seen in the case of the stabilized sludge. The specific conductance of the initial leachate from the untreated, ponded, and oxidized sludge was much higher but improved with total leaching time and total leachate volume so that the specific conductance of the leachates of the other sludges fell within the same range as that of the stabilized sludge and natural gypsum after two or three shake cycles. The lower specific conductance in the Columbus-Southern Ohio (CSO) leachate after two 72-hr leach cycles was due to the low solubility of $CaSO_3$, which was the predominant species in the untreated fly-ash-free CSO sludge. Both FBC and FGD leachates exceed the TDS for DWS.

One must keep in mind that the leachate characteristics presented in Figures 23 and 24 are of vacuum-filtered and dried sludge. The supernatant liquors of the sludges had much higher TDS and specific ion concentrations, as seen in Table 37, which summarizes the chemical characteristics of the dried solids and the original liquor, as well as the

Table 37

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CHEMICAL CHARACTERISTICS OF FGD SLUDGE, LIQUOR, AND LEACHATE[a]

Substances	Sludge, ppm[a] (on dry basis)	Liquor, ppm			Leachate from dried solids, ppm (after 200-hr continuous shake)				DWS, mg/ℓ
		Untreated	Ponded	Oxidized	Untreated[a]	Ponded[b]	Oxidized[c]	Stabilized[d]	
Al	0.2 - 20%	< 2	0.4	20	< 1	< 1	< 1	< 1	
Ag	< 1	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	0.05
As	3 to 30	0.03	0.03	0.01	▨ 0.01 to 0.06	▨ 0.09	0.01	0.05	0.05
B	30 to 300	1 to 20	> 7	> 20	0 to 2	> 3	> 1	1	
Ba	10 to 1000	< 1	< 1	< 1	< 1	< 1	< 1	< 1	1.0
Be	0 to 15	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.01	< 0.1	
Bi	< 10	< 0.02	< 0.02	< 0.02	< 0.01	< 0.01	< 0.01	< 0.01	
Ca	10 to 30%	▨ 500 to 1500	▨ 1924	▨ 2406	▨ 300 to 1000	▨ 760	▨ 160	▨ 630	200
Cd	< 3	< 0.01	< 0.02	▨ 0.2	< 0.01	< 0.01	< 0.01	< 0.01	0.01
Co	0 to 10	< 0.05	< 0.05	< 0.06	< 0.05	< 0.05	< 0.05	< 0.05	
Cr	1 to 100	< 0.04	< 0.03	< 0.06	< 0.03	< 0.03	< 0.03	< 0.03	0.05
Cu	1 to 60	< 1	< 1	< 1	1	< 1	< 1	< 1	1.0
Fe	0.1 to 10%	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	< 0.3	0.3
Hg	0.1 to 3	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	< 0.002	0.002
Mg	0.1 to 10%	▨ 0 to 600	< 30	▨ 1104	▨ 10 to 250	< 30	▨ 200	16	150
Mn	10 to > 1000	▨ 0 to 0.07	0.02	▨ 20	< 0.05	< 0.05	< 0.07	< 0.05	0.05
Mo	0 to 20	< 0.5	7	0.7	< 0.2	< 0.2	0.1	0.3	
Na	0.01 to 5%	0 to 100	111	106	5 to 15	5	3	6	
Ni	0 to 30	< 1	< 1	< 1	< 0.05	< 0.05	< 0.05	< 0.05	2.0
Pb	0 to 200	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	< 0.05	0.05
Sb	< 33	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	< 0.5	
Se	1 to 5	▨ 0.005 to 0.03	0.01	▨ 0.32	▨ 0.01 to 0.03	0.007	▨ 0.1	0.006	0.01
Si	0.5 to 20%	2 to 20	2.7	5	0.1 to 4	2	1	3	
Sn	< 10	< 1.0	< 1.0	< 1.0	< 0.05	< 0.05	< 0.05	< 0.05	1.0
Sr	100 to 1000	< 2	> 7	40	< 1	1	2		
Ti	100 to > 1000	< 1	< 1	< 2	< 1	< 1	< 1	< 1	
V	0 to 100	< 0.05	2	< 0.06	< 0.05	< 0.05	< 0.05	< 0.05	
Zn	20 to 200	< 3	< 3	< 3	< 3	< 3	< 3	< 3	5.0
Zr	1 to 1000	< 2	< 2	< 2	< 1	< 1	< 1	< 1	
CO_3	0.1 to 15%								
SO_3	0.05 to 90%	0 to 40	< 10	< 10	< 10	< 10	< 10	< 10	
SO_4	3 to 65%	▨ 1000 to 7000	▨ 1200	▨ 1450	▨ 500 to 2500	▨ 1700	▨ 1500	▨ 1400	250
Cl	0 to 1%	▨ 300 to 1000	▨ 2800	▨ 5100	30 to 120	180	170	2	250
Br		0 to 40			0 to 3			< 1	
F	10 to 90	▨ 2 to 23	▨ 22	▨ 33	▨ 1 to 6	1.3	▨ 4.5	▨ 5	2.4
NO_3 (as N)		▨ 0 to 100	< 10	▨ 90	< 10	< 10	< 10	< 10	10
NO_2		0 to 40			< 10			10	
PO_4		0 to 10			< 1			< 1	
TOC		< 30	< 30	< 30	< 30	< 30	< 30	30	
pH		▨ 8 to 10	6.6	▨ 6.1	7.5 to 8.5	8.0	8.2	8.0	6.5 to 9.2
Sp. Cond. (μmho/cm)		▨ 4000 to 9000	▨ 9920	▨ 16900	▨ 2000 to 3000	▨ 2640	▨ 2930	▨ 2350	~750

(a) Range of 3 untreated sludge samples (LGE, CSO, DLC)
(b) 1 ponded sludge sample (TVA)
(c) 1 oxidized sludge sample (TVA)
(d) Chemically treated by Dravo's "Calcilox"
▨ exceed drinking water standards (NIPDWR, USPHS and WHO)

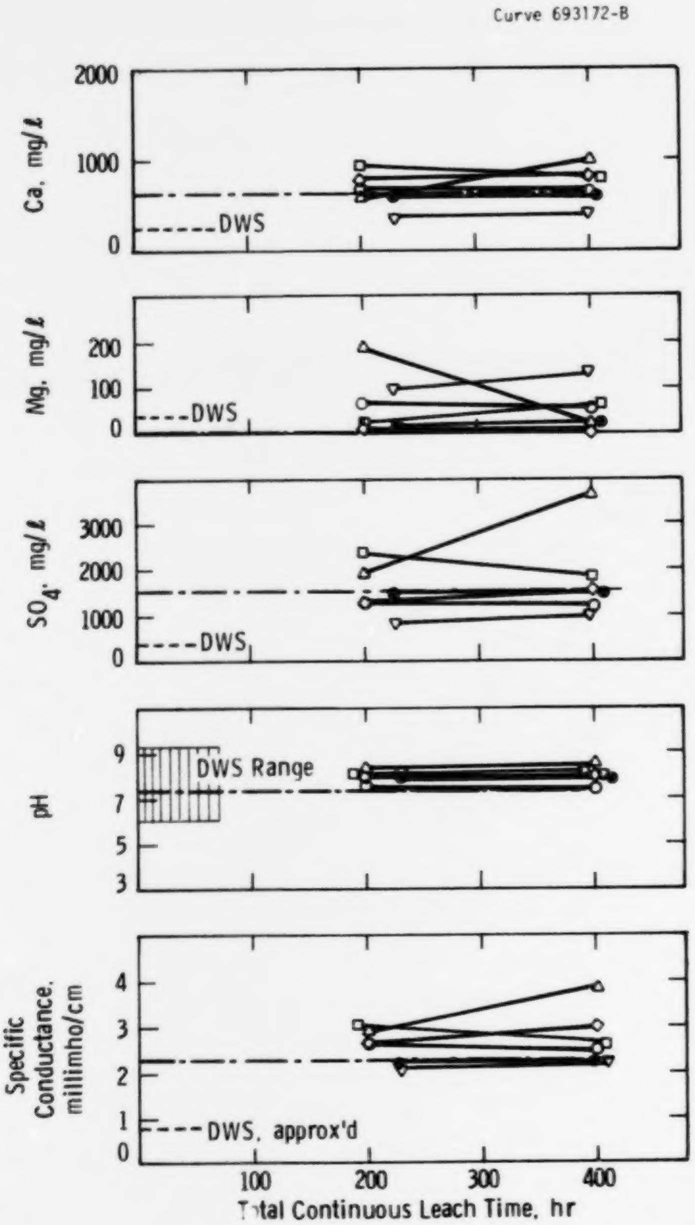

Figure 23 - Leachate Characteristics of Dried FGD Sludge as a Function of Continuous Leaching for:

△ LGE Untreated
▽ CSO Untreated
□ DLC Untreated
◊ TVA Ponded
○ TVA Oxidized
● Calcilox - Stabilized
-·—·—·— Natural Gypsum
- - - - - - - - - DWS

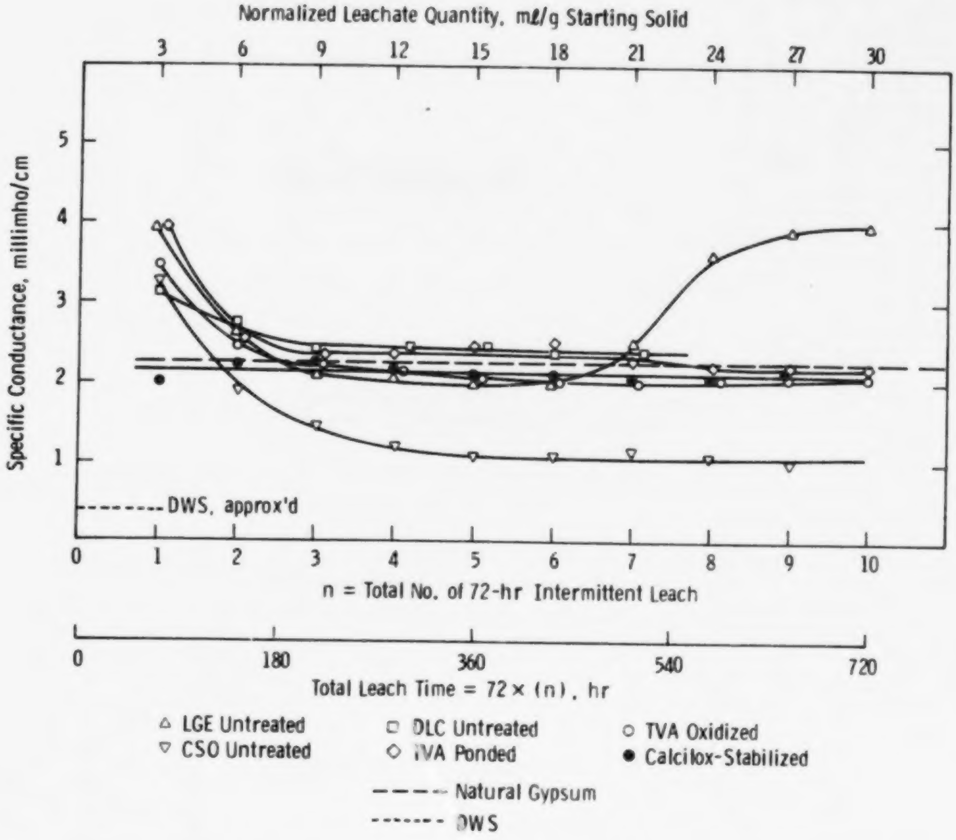

Figure 24 - Leachate Characteristics of Dried FGD Sludge as a Function of Intermittent Leaching

leachate following the 200-hr continuous shake test. The trace elements are lowest in the leachate of stabilized sludge. Although oxidation to gypsum increased the crystal size and improved the sludge setting property and shear stress,[39] it did not appear to significantly affect trace element concentrations in the leachate. As expected, in all cases the original liquor was of poorer quality than the leachate from the dried sludge.

COMPARISON WITH FBC RESIDUE

Figure 25 compares the leachate quality as indicated by the specific conductance as a function of the intermittent shake cycle for the spent

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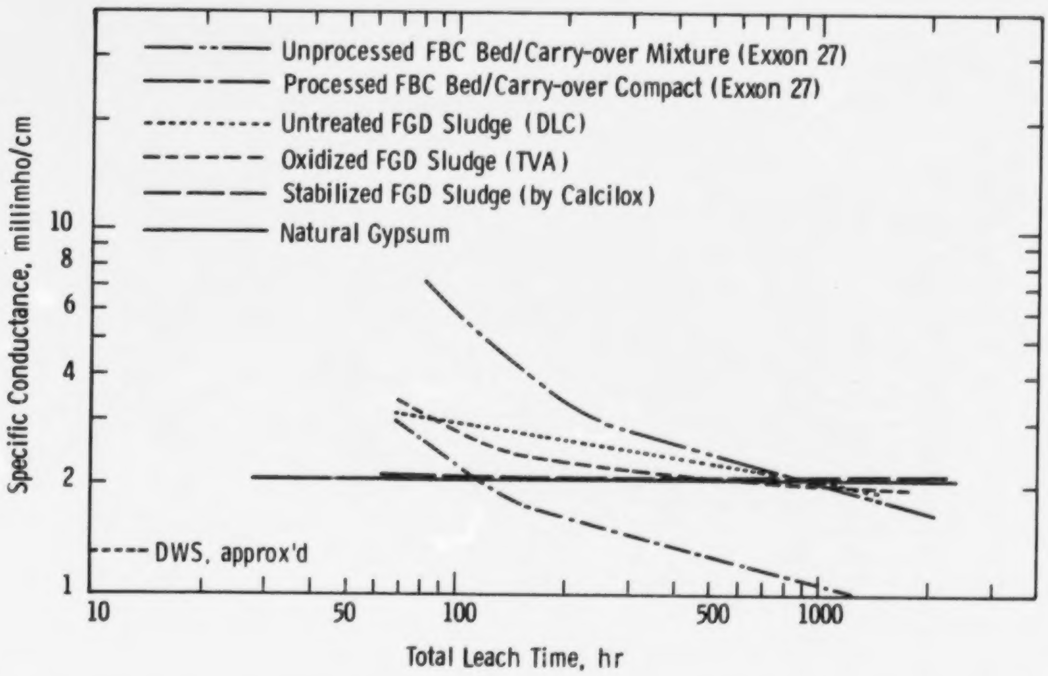

Figure 25 - Comparison of Leachability of Processed and Unprocessed FGD and FBC Waste with Natural Gypsum

FBC solids (unprocessed and processed bed/carry-over mixtures), FGD sludges after drying (untreated, oxidized, and stabilized), and natural gypsum.

A further comparison of FBC and FGD leachates (including major and trace species, pH, TDS, and TOC) is shown in Table 38, which summarizes Table 37 and the analogous tables for unprocessed FBC residue presented earlier in this section.

Several points can be noted in Figure 25. First, as discussed previously, processing of FBC residue improves the leachate quality to a level equal to or better than the natural gypsum leachate. The leachate from both the processed and unprocessed FBC residue improves with total leachate volume passing through the sample and total leaching time. Although lower initially, the leachability of natural gypsum is constant throughout the 15 72-hr cycles tested. Similarly, both oxidation and

Table 38

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COMPARISON OF LEACHATE CHARACTERISTICS OF THE FBC AND FGD RESIDUES

Substance	Original FGD Liquor, ⓐ mg/ℓ	Leachate, mg/ℓ			Drinking Water ⓔ Standards, mg/ℓ
		FBC ⓑ	FGD ⓒ	FGD (stabilized) ⓓ	
Al	0 to 20	0 to > 2	< 1	< 1	
Ag	< 0.05	< 0.05	< 0.05	< 0.01	0.05
As	< 0.05	< 0.05	▨ 0 to 0.1	0.05	0.05
B	> 5	0 to > 5	> 1	1	
Ba	< 1	< 1 ⓕ	< 1	< 1	1.0
Be	< 0.02	< 0.02	< 0.02	< 0.1	
Bi	< 0.04	< 0.04	< 0.04	< 0.04	
Ca	▨ > 500	▨ > 500	▨ > 500	▨ > 500	200
Cd	▨ 0 to 0.2	< 0.01	< 0.01	< 0.01	0.01
Co	< 0.1	< 0.1	< 0.1	< 0.1	
Cr	< 0.05	< 0.05 ⓕ	< 0.05	< 0.05	0.05
Cu	< 1	< 1	< 1	< 1	1.0
Fe	< 0.3	< 0.3 ⓕ	< 0.3	< 0.03	0.3
Hg	< 0.002	< 0.002	< 0.002	< 0.002	0.002
Mg	▨ 0 to > 1000	< 30 ⓕ	▨ 0 to 500	16	150
Mn	▨ 0 to 20	< 0.05 ⓕ	▨ 0 to 0.1	< 0.05	0.05
Mo	0.1 to 7.0	< 5	< 1	< 1	
Na	0 to > 100	0 to > 100	< 30	6	
Ni	< 1	< 0.1	< 0.1	< 0.1	2.0
Pb	< 0.05	< 0.05	< 0.05	< 0.05	0.05
Sb	< 0.5	< 0.5	< 0.5	< 0.5	
Se	▨ 0.001 to 0.5	< 0.01 ⓕ	▨ 0 to 0.1	0.006	0.01
Si	0 to 30	0 to 30	0 to 5	3	
Sn	< 1.0	< 1.0	< 1.0	< 1.0	1.0
Sr	0 to 40	0 to > 10	0 to 5		
Ti	< 2	< 2	< 2	< 2	
V	< 2	< 1	< 1	< 1	
Zn	< 3	< 3	< 3	< 3	5.0
Zr	< 2	< 1	< 1	< 1	
SO_3	< 10 to 40	< 10	< 10	< 10	
SO_4	▨ 1000 to 7000	▨ 1000-2000	▨ 1000-3000	▨ 1400	250
Cl	▨ 300 to 6000	< 250 ⓕ	▨ 30 to 300	2	250
F	▨ 10 to 50	< 2.4 ⓕ	▨ 1 to 10	▨ 5	2.4
NO_3 (as N)	▨ 0 to 100	< 10	< 10	< 10	10
TOC	< 30	< 30	< 30	< 30	
pH	▨ 6 to 10	▨ 9 to 12	6 to 9	8.0	6.5 to 9.2
TDS	▨ 5000 to 14000	▨ 2000 to 4000	▨ 2000 to 3000	▨ 2000 to 2500	500
Specific Conductance, millimho/cm	5.0 to 17.0	0.5 to 10.0	2.0 to 3.0	2.35	

ⓐ Liquor obtained from filtration of 5 FGD sludge samples (untreated, ponded, oxidized)

ⓑ The figures in the FBC column include the full range of data reported previously in this section and in Ref. 17 for 30 unprocessed FBC residues, including both spent bed material and carry-over

ⓒ Leachate from dried FGD sludge — untreated, ponded, oxidized (range of 5 samples)

ⓓ Leachate from dried FGD sludge — stabilized with Dravo's "Calcilox" (1 sample)

ⓔ NIPDWR, USPHS and WHO Drinking Water Standards

ⓕ Drinking Water Standards met by leachate from all 30 FBC residues tested except for 2 batches carry-over fines

▨ Exceed Drinking Water Standards

stabilization of the FGD sludge improve the leachate quality. We can say that, on the average, the TDS in the leachate of FBC and FGD residues are within a range similar to that of natural gypsum. The liquor of FGD sludge, however, contains much higher TDS, major species, and trace elements, as shown in Table 38.

Since the leaching tests were conducted on the dried sludge following vacuum filtration, the actual initial leachate quality from the FGD sludge would be worse than that shown here because of the presence of sludge liquor even in the dewatered sludge (∿50 percent solid). Table 38 shows that the FGD liquor contains much higher dissolved major and trace species than the leachate of the dried sludge solid, as expected. The trace elements in FGD leachate are further reduced by stabilization.

Table 38 shows that both the FBC and the stabilized FGD residues have leachates that generally pass the DWS for trace metal elements. Leachate from both FBC and FGD residues have high calcium, SO_4, and TDS, as does leachate from natural gypsum. The leachate of FBC residues has high pH. In addition to the major species, some minor and trace element concentrations in the leachate from the dried, nonstabilized FGD sludge tested here exceeded the DWS, notably magnesium, chlorine, fluorine, manganese, arsenic, and selenium, although further testing of additional FGD samples would be necessary to confirm the point.

The comparison between the FBC and FGD residues presented in this section has been limited to their chemical and leaching properties. The physical properties of the FGD sludge are reported in the literature.[38-40]

8. SPENT SORBENT PROCESSING

REVIEW OF PROCESSING OPTIONS

The previous sections have dealt with the potential environmental impact of FBC residues, emphasizing the response of unprocessed residues to leaching with aqueous solutions. We have conducted other studies to identify processes that could minimize such impact if required for specific applications or could result in further resource utilization. These studies, described in this report, represent an extension of prior work at Westinghouse, under contract to EPA, which is also reviewed.

The new material presented extends the investigation into producing solid compacts as an environmentally acceptable disposal method for FBC residues. The major portion is concerned with obtaining further data on the long-term stability of the compacts, and another section deals with a method for direct disposal of FBC residues for utilization as fine aggregate in concrete. Finally, we present an analysis of selected leachate data with an interpretation applicable to a full-scale residue disposal operation.

Perspective on Residue Processing

For the most part FBC residues will be produced at elevated temperature (300-900°C). Even in the case of direct disposal, some on-site processing equipment will be required to permit safe handling of these residues. This equipment will include conveyors, coolers, and probably enclosed storage silos. For our purposes processing means those operations beyond simple cooling and transport and will include, for example, blending, grinding, and sieving. Other operations may also be involved, depending on the particular process option under discussion.

The specific questions that arise concerning the direct placement of FBC residues in the environment include the amount and quality of leachate produced when the residue contacts precipitation or groundwater, the amount of heat released, and the amount of fugitive dust emitted. The environmental question, therefore, can be formulated as what method of disposal will offer the least environmental degradation for the longest period of time and for the lowest cost?

Processing FBC residues is under investigation because it may provide alternatives to direct disposal that:

- Could minimize negative environmental impact, or
- Might result in recovering a useable resource.

Numerous processing options have been identified,[5,6] and these may be grouped under two main headings:

- Processing for disposal
- Processing for utilization.

Although many of these are under investigation, the work at Westinghouse has focused on low-temperature (below 100°C), simple, physical processes. We have deferred work on high-temperature processes because we anticipate that the additional energy requirement of such processes would make them less attractive economically.

Another consideration in the Westinghouse development program was the planning horizon. Some processes might be developed in 1 to 3 years, while others might require 10 to 20.

Because of the large tonnage of residues that can be produced in large-scale FBC systems, processing for utilization offered the possibility of minimizing environmental problems and enhancing system economics at the same time. On the other hand, to demonstrate the reliability of physical and mechanical properties, conformity to (new) standards and specifications, and market acceptance would have required a commitment in time far beyond the scope of the previous contract.

We have, therefore, given greater attention to processing for disposal. The technical criteria applicable to this group of processes are expected to be fewer and less restrictive than for the other group, which results in a product for the commercial market.

Specific alternatives to direct disposal include landfill, road base material, treatment of acidic wastes as acid mine drainage, agriculture, and coarse aggregate. In the case of direct disposal, as in unlined ponds, the residues would remain as a potential source of leachate indefinitely into the future and would represent a continuing potential for degradation of groundwater by permeation and of surface waters by overflow. Membrane-lined ponds eliminate the former hazard but only for the life of the membrane - some 20 years. Then, action would be required to control potential leachates to specified standards. Clay-lined ponds might appear to be longer lived, but such liners are subject to cracking by earth movements and deterioration from chemical interactions with soil. Further, suitable clays are not usually located near the site of the pond.

In contrast, use of the alkaline FBC residues in treating acid mine drainage would simply transfer the solids disposal problem to another location even if this treatment were successful.

Investigation of agricultural uses is being investigated by the Department of Agriculture and was considered outside the scope of the existing contract.

Review of Previous Work

Westinghouse Feasibility Tests

Work reported in 1978[5] had been directed toward establishing the feasibility of disposing of FBC residues as landfill, coarse aggregate, or road base material. Such use implies minimal on-site processing coupled with finality of disposal.

Westinghouse demonstrated that stable solid compacts could be produced from blends of FBC spent bed material and conventional coal ash at ambient temperature and pressure. By converting the granular residues into larger masses, one would reduce the surface-to-volume ratio, thereby reducing potential leachate production when the residues were placed in the environment. If a given mass of residue consisting of N particles of particle density ρ_o is processed to a single mass of density ρ, the total external surface is reduced by the ratio $L_o\rho_o/L_\rho$, where L is a characteristic dimension. Since spheres and cubes have the minimum surface-to-volume ratio for curved and rectilinear shapes respectively, L here refers to the length of either the diameter of a sphere or the edge of a cube. Thus, if the density is essentially unchanged by the size increase process, a 10-fold increase in particle size is accompanied by a 10-fold decrease in surface area.

For porous particles, the internal surface of the pores can be many times the external surface area. Two situations then arise. In one, the pores permit flow into and possibly through the particles. This is considered to be unusual. In the other and more likely case leaching involves diffusion of solute from within the particle through stagnant films and thence out through the pores to the bulk leaching medium surrounding the particles. It is of interest, therefore, to demonstrate whether internal pore surface in FBC residues contributes significantly to leachate constituents, whether pore surface is reduced by the process of forming the residues into larger masses, and whether the larger masses are environmentally stable to:

- Cycles of hydration and drying
- Cycles of freezing and thawing
- Attack by chemical agents, such as sulfates and chlorides.

The third action is relevant to ocean disposal as well as to disposal on land in sites where contact with natural brines is possible.

Stability is an important property, for if the compacts should break down into smaller fragments on aging, freezing and thawing, hydrating and drying, crushing under load, or reacting with other substances, the reason for making them could be negated.

Feasibility tests were conducted in the laboratory using PFBC residues from the Exxon pilot plant to cast 5-cm cubes from a mix of ground bed material, carry-over, and water. The result was stable, solid compacts that had compressive strengths up to about 15 MPa (2175 psi). Higher strengths (90 MPA or 13,000 psi) were obtained by isostatically pressing Exxon spent sorbent ground to -125 μm and then water curing it for 14 days. We concluded that the residues displayed sufficient pozzolanic activity to warrant further investigation of the processing options identified above.

In parallel with this early laboratory work, we reviewed relevant literature for information applicable to our studies. We were specifically interested in data on composition limits, processing methods, and performance.

Literature Study

One of the areas of relevant technology we reviewed was the utilization of other sulfate wastes. Smith, et al.,[41] in work sponsored by the Federal Highway Administration, had tested sulfate wastes from FGD scrubbers, hydrofluoric acid manufacture, titanium dioxide extraction, steel pickling liquor neutralization, and acid mine drainage neutralization. The purpose of their work was to determine whether treatment of these wastes would result in materials useful for road construction. Included in the tests were determinations of the effects of water content, lime type, sulfite vs. sulfate, lime/sulfate ratio, fly ash content, sulfate content, and Portland cement addition on the mechanical properties of the processed wastes.

Useful indications were that the water content could be perhaps as low as 18 percent, that calcitic lime is better than dolomitic lime, that sulfite and sulfate results were roughly equivalent, that an optimum lime-sulfate ratio exists at about 1:1, and that a gypsum content of up to 10 to 20 percent favored higher compressive strengths. X-ray examinations were attempted but were inconclusive. One sulfite sludge mix developed a compressive strength of about 11 MPa (1600 psi). Strengths for all mixes increased on aging to 91 days. Permeability was reduced for some of the mixtures to as low as 1×10^{-6} cm/s. Freeze-thaw resistance was poor - few cycles, low strength.

Since these studies basically dealt with lime/silica reactions, we concluded that we could expect some similarity in our FBC work. For example, water is an essential ingredient of concrete, but the evidence is that it should be minimized to achieve maximum strength and environmental stability. The figure of 18 percent noted above is less than the theoretical for hydration of Portland cement (24 wt %). The lowest value of water used in Westinghouse screening tests was 30 percent. The Smith work suggested that future Westinghouse tests could aim for a lower water content.

The gypsum content Smith found was much higher than that of Portland cement (5.1 wt % $CaSO_4$). This supported earlier Westinghouse results that $CaSO_4$ content greater than 3 percent was not detrimental to compressive strength. Ideally, for a once-through process FBC residue would be a mixture of coal ash and lime that had been sulfated 100 percent. For a 3 percent sulfur, 10 percent ash coal, the $CaSO_4$ content at 90 percent sulfur capture would be 51 percent of the solid residues. This suggests that fixed FBC residues might have lower compressive strengths when lime is minimized. These strengths might be acceptable if the fixed residues are merely discarded to the environment, but higher values might be sought through adjustment of the residual CaO content if the fixed residues are to be utilized.

In other work, done by Dunstan[42] through the Bureau of Reclamation, substitution of 15 to 25 wt % of Portland cement by lignite and subbituminous fly ashes yielded concretes with acceptable freeze-thaw resistance and compressive strengths but with inadequate sulfate resistance. The effect of iron oxide content appeared to merit investigation.

With respect to test methods and commercial specifications, P. W. Brown of the National Bureau of Standards[43] found that existing tests for materials may represent obstacles to the use of FBC residues in the construction industry in that the tests may be inadequate, biased, or not representative of field conditions. Existing specifications may also favor suppliers of conventional materials. These conclusions helped shift the focus of the Westinghouse residue processing studies from utilization to disposal.

Performance Criteria

Whatever the form into which FBC residues are processed, there will be environmental constraints that must be met. This is true whether the processed residues are deposited in the environment or are utilized in some way in the environment. The effort to define adequate environmental protection in legal and practicable terms is a continuing one, and so the statements of performance criteria given here are subject to change.

1. The processed residues should not release substances that can migrate to and enter natural water supplies in concentrations in excess of accepted water quality standards applicable to the water use involved (drinking water, agriculture, industry) at the point of use.
2. The processed residues should conform to all standards or regulations on fugitive dust, odor, or other considerations.
3. The processed residues should have sufficient physical and chemical stability so that environmental actions such as wetting, drying, freezing, thawing, or contact with other natural substances in the environment will not impair their performance under Item 1 above.

Other performance criteria will be added to this list if the FBC residues are processed for utilization.

PRESSED MATERIAL

General

We have hypothesized that the binding forces in FBC compacts are similar to those in normal Portland cement concrete. Others have established that hydration of di- and tricalcium silicates is mainly responsible for the compressive strength developed in cement and concrete. Compressive strength also appears to correlate with other properties such as splitting tensile strength and therefore represents an easily measured parameter for screening the effects of several variables. Hydration of other compounds, such as tricalcium aluminate (C_3A) and tetracalcium aluminum ferrite (C_4AF), where $C = CaO$, $A = Al_2O_3$, and $F = Fe_2O_3$, has been shown to result in compressive strengths much lower than those of the hydrated calcium silicates, as discussed later in this report.[44]

Objective

The feasibility of preparing solid compacts from FBC residues was demonstrated in the previous work. The objective of the current work is to obtain evidence that these compacts do have long-term environmental stability. Several measures might have been investigated, but budget constraints dictated that only one be selected at this time. We decided to concentrate on freeze-thaw resistance because the compacts would more certainly be exposed to temperature changes in an actual plant than to sulfates and because freeze-thaw cycling was considered a severer test than simple wetting and drying.

Test Plan

Variables potentially affecting the stability of the compacts and possibly also the composition of leachate producible from them included:

- Type of sorbent - limestone, dolomite
- Source of sorbent - crystal size, porosity
- Chemical composition of sorbent
- Particle size distribution of sorbent
- Sorbent/fuel treat ratio in FBC process
- Sulfur capture achieved in FBC process
- Residence time of sorbent in FBC process
- Ash content of fuel
- Chemical composition of fuel ash
- Water content of compacts
- Curing time and curing temperature for the compacts
- Composition of the compacts - spent sorbent, fuel ash, other materials.

Since the main FBC process is still under development, no one sorbent has emerged as the one to be used on a commercial scale. The test plan, therefore, was designed to cover a range of compositions in an attempt to bracket future design values. One constraint adopted was process simplicity. Rather than have a separate disposal process for spent sorbent and fuel ash, we decided to aim for a single process through which all sorbent/fuel solid residues could be disposed of. This meant fixing the ratio of feed rates to the disposal process for the two residues at production proportions. Further discussion is given in a later section of this report.

Solid state reactions are involved, and therefore the effect of particle size distribution was included in the test plan. On the basis of previous work, we selected two size ranges: -125 +44 µm and -44 µm. The latter reflects commercial practice in the cement industry. Because grinding energy increases rapidly as particle size desired decreases, the former size range represents a compromise in reactivity as grinding energy.

In most of the previous FBC residue processing work,[5,34] wet-casting at ambient pressure and temperature were used. This approach is similar to the casting of cement and results in the phenomena of setting and hardening as in cement. We believe that similar phenomena would occur naturally in an FBC residue disposal site operated to promote this type of fixation processing. Since freeze-thaw cycling was expected to be a severe test, we decided to select a method of preparing specimens that would maximize the probability of their surviving the tests. Isostatic pressing was chosen over direct casting because it led to specimens with a much higher compressive strength. If these specimens failed, then direct casting would also be questionable as a method for making specimens with long-term stability; if they survived, then other compaction methods more suited to commercial-scale operation, such as briquetting or tabletting, would be investigated. The use of pressed compacts might also give information on the leaching properties of construction blocks or other similar items fabricated from FBC residues.

Test Materials

Spent bed material was obtained from the Exxon, the PER, and the B&W pilot plants. Chemical analyses are reported in Table 39.

The PER stone was a high-silica, high-alumina lime in which the calcium was about 50 mole % sulfated. The B&W stone was a low-silica, low-iron, low-alumina lime that was about 20 mole % sulfated. The Exxon stone was a dolomitic lime with about 50 mole % of the calcium in the bed material sulfated. Since all of these specimens were exposed to elevated temperatures and since the loss on ignition for the pilot plant materials was no greater than 4.23 percent, we judged the residual carbonate content (as $CaCO_3$) to be negligible. In more definitive tests

Table 39

CHEMICAL ANALYSES OF FBC PILOT PLANT RESIDUES

Source Material	Duquesne Fly Ash[a]	PER Bed	Exxon Run 43.3 Bed	Exxon Run 43.3 Carry-over	B&W Run 19 Bed
Composition, wt %					
CaO	0.4	28.84	38.64	15.62	67.01
MgO	1.0	2.13	13.25	7.70	1.25
SiO_2	44.9	27.20	8.60	29.40	3.90
Al_2O_3	19.1	10.26	5.70	11.20	5.55
Fe_2O_3	9.6	5.39	3.95	8.80	2.00
SO_3	--	19.90	29.00	16.38	19.09
LOI	14.0	1.04	0.32	4.23	0.51
Other	11.0	5.27	0.44	6.67	0.69
	100.0	100.00	100.00	100.00	100.00
Composition, moles/100 g					
CaO	0.0071	0.5142	0.6890	0.2785	1.1949
MgO	0.0248	0.0528	0.3287	0.1910	0.0310
SiO_2	0.7472	0.4526	0.1431	0.4893	0.0649
Al_2O_3	0.1873	0.1006	0.0559	0.1098	0.0544
Fe_2O_3	0.0601	0.0338	0.0247	0.0501	0.0125
SO_3	--	0.2486	0.3635	0.2046	0.2384
Molar ratios					
SO_3/CaO	--	0.0435	0.5276	0.7346	0.1995
CaO/SiO_2	0.0095	1.1361	4.8148	0.5692	18.4114
Net CaO/SiO_2[b]	--	0.5868	2.2746	0.1510	17.738

---

[a] Fly ash from a conventional boiler plant at the Elrama, PA station of Duquesne Light Company.

[b] Net CaO = CaO less SO_3.

the amount of residual carbon, rather than carbonate, would be determined specifically because carbon laydown on particle surfaces might affect reactivity of the bed material more than the presence of inert carbonates.

Preparation of Test Materials

The FBC residues were ground to -125 and -44 μm (-120 and -325 mesh) by outside contractors. The Duquesne fly ash was not ground because typically it is 95 percent through 149 μm (100 mesh). Upon return to Westinghouse, each size fraction was blended for uniformity. Quantities available were as follows (kilograms):

Sorbent Source	Particle Size Range, μm -1255 +44	-44
PER	88	52
B&W	56	36
Exxon	80	47

A check of the particle size distribution of the -44 μm (-325 mesh) fraction from the B&W stone showed only 24 percent through 44 μm (325 mesh). Since particle size was identified as an important variable, we judged it necessary to explain this discrepancy. One possibility was water absorption, which would lead to swelling of the particles and possibly also agglomeration.

Thermogravimetric analysis showed an 8.65 percent drop in weight when the stone was heated in nitrogen to 1000°C. Slight slope changes occurred at 390°C and at 660°C. About half of the total weight loss was attributed to water; the balance may be CO_2. Data on weight loss at 700 and 1000°C for four samples of ground sorbent are in Table 40. Heating the sorbent to 700°C should drive off the surface moisture and water of hydration of gypsum and $Ca(OH)_2$. We concluded that a significant amount of water was present and, therefore, ground B&W spent bed material tended to pick up water on exposure to ambient air.

Table 40

WEIGHT LOSS ON HEATING GROUND B&W SPENT BED MATERIAL

Size Range, μm	Location in Drum	% Loss @ 700°C	% Loss @ 1000°C
-125 + 44	Bottom	4.50	6.13
	Middle	2.14	2.57
-44	Bottom	7.38	8.65
	Middle	7.28	9.85

Next, the particle size distribution of the -44 μm (-325 mesh) fraction of the ground B&W stone was checked by means of an Alpine Model 200 Air-Jet Sieve. The procedure is given in Appendix A. One sample was from the material as received from the outside grinders and the other from a -63 μm (-230 mesh) fraction sieved by Westinghouse from this material. The results are in Table 41. Another sample of the as-received -44 μm material was dried at 600°C for 30 minutes and then examined by Coulter Counter. The medium used was Isoton and 30 percent glycerine. These results are in Table 42 and are plotted along with the data of Table 41 in Figure 26.

Since the drying process was accompanied by a shift in particle size distribution to smaller sizes, we concluded that the finely ground materials were at least hygroscopic, most likely because of the free CaO present. The effect is to increase particle sizes. The question remained, however, of whether the material had actually been ground to 100 percent through -44 μm (-325 mesh). Rather than complicate the test procedure with a drying step, we decided to screen the nominal -44 μm (-325 mesh) fraction to obtain an actual -63 μm (-230 mesh) fraction for use in the freeze-thaw tests. The quantity prepared was 3000 g; its size distribution is given in Table 41.

Table 41

PARTICLE SIZE ANALYSIS OF AS-RECEIVED -44 μm (-325 mesh) B&W RUN 19 SPENT BED MATERIAL USING AN ALPINE AIR-JET SIEVE

Sieve Size, μm	Weight % Retained on Indicated Sieve	
	As Received	-63 μm (-230 mesh) Fraction
150	0.0	0.0
105	4.5	0.0
74	30.0	0.0
63	46.0	0.0
45	59.5	1.0
32	74.0	6.0
20	80.2	56.4
10	98.8	94.3
5	100.0	99.4

Preparation of Test Specimens

Previous work on direct casting of 5-cm cubes from blends of Exxon residues had indicated that 15 weight % carry-over on total solids was near the optimum amount, as reflected in compressive strength. Initial attempts to extend this work by use of isostatic pressing of dry mixes failed. Details of this procedure are given in Appendix B. The dry mix is placed in a mold, subjected to hydrostatic pressure of 138 MPa (20,000 psig) for 1 minute, removed from the mold, cured in water for 24 hours, cut into desired lengths, and then placed under water for completion of curing.

Since carry-over was not available for all three pilot plant residues, these initial tests were conducted with blends of spent bed material and Duquesne fly ash. All specimens, however, fell apart when cured in water. One specimen prepared with Wyoming lignite fly ash also crumbled in water.

Table 42

PARTICLE SIZE ANALYSIS OF AS-RECEIVED −44 μm B&W RUN 19 SPENT BED MATERIAL USING A COULTER COUNTER

Diameter, μm	Weight % greater than Indicated Diameter
2.52	100.0
3.17	97.1
4.00	94.9
5.04	92.1
6.35	88.7
8.00	84.0
10.08	79.0
12.7	73.8
16.0	67.8
20.2	61.2
25.4	57.1
32.0	52.3
40.3	46.8
50.8	39.5
64.0	28.4
80.6	22.3
101.6	11.9
128	5.4
181	2.5
203	0.0

Note: Sample dried at 600°C for 30 minutes.

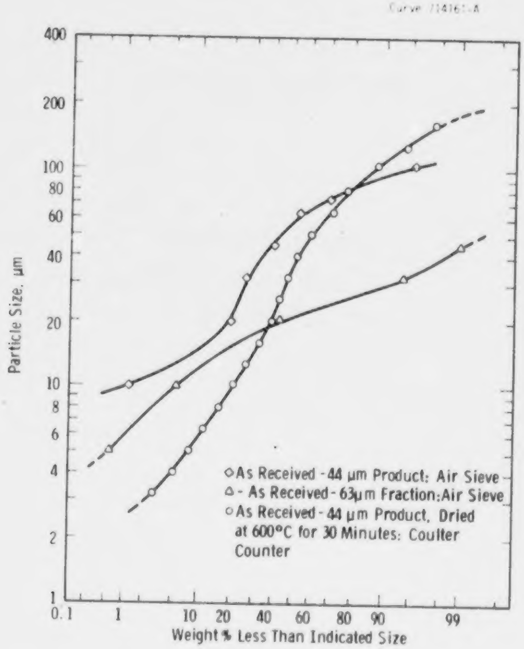
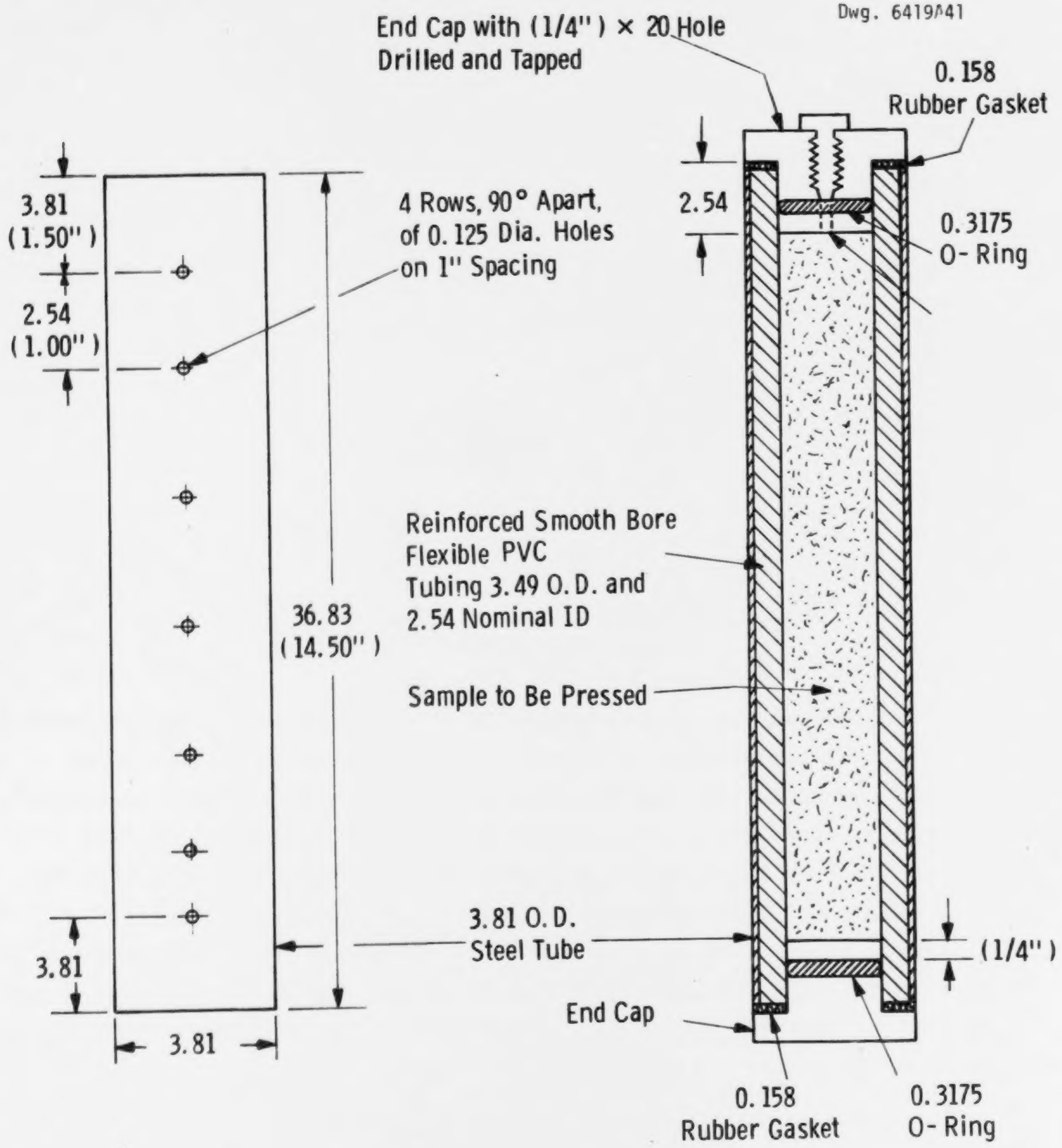


Figure 26 - Particle Size Distribution of Ground B&W Spent Bed Material from Run 19

We interpreted this as indicating the need for preslaking the residues. One method was to slake the bed materials and carry-over specimens separately, dry them at 100°C, and set them aside. Since this step represented an undesirable complication of the contemplated disposal process, we decided to test the materials separately, beginning with the bed material. Because of constraints of time, funding, and material available, a sequential test plan was evolved, the first stage of which was freeze-thaw tests on isostatically pressed ground spent bed material. Subsequent tests were to be devised on the basis of the results from this stage.

Because of the number of test specimens required, we developed a larger mold for use in isostatic pressing. Figure 27 is a diagram showing details of the mold assembly used to prepare the specimens, while Figure 28 is a photograph of the mold. The cylindrical specimens


Dwg. 6419A41
End Cap with (1/4") × 20 Hole Drilled and Tapped
0.158 Rubber Gasket
3.81 (1.50")
2.54 (1.00")
4 Rows, 90° Apart, of 0.125 Dia. Holes on 1" Spacing
2.54
0.3175 O-Ring
Reinforced Smooth Bore Flexible PVC Tubing 3.49 O.D. and 2.54 Nominal ID
36.83 (14.50")
Sample to Be Pressed
3.81
3.81 O.D. Steel Tube
(1/4")
3.81
End Cap
0.158 Rubber Gasket
0.3175 O-Ring

Note: Dimensions in Centimeters except as noted.

Figure 27 - Mold Assembly for Preparation of Specimens by Isostatic Pressing (Drawing not to Scale)

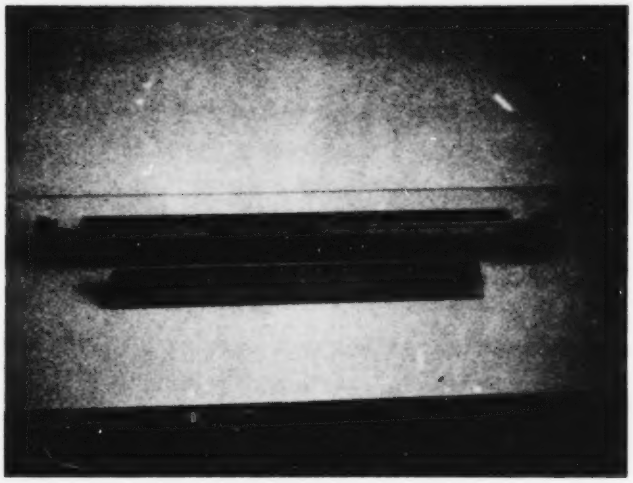


Figure 28 - Mold Assembly

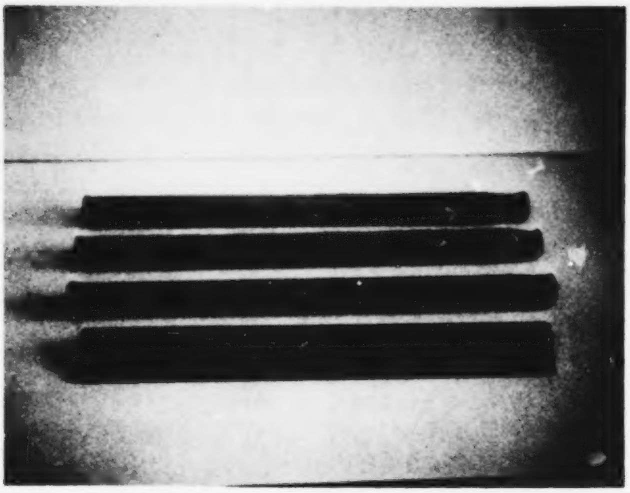

B&W
Exxon
PER

Figure 29 - Specimens Produced by Isostatic Pressing

produced were about 1.8 cm in diameter and 25 to 50 mm long. Figure 29 shows typical specimens. From these were cut the actual test pieces, which were about 3.7 cm long (1.5 in). All of the test specimens pressed from ground bed material as well as the control specimens were successfully cured in water for 14 days.

Test Apparatus

Figures 30 and 31 show details of the apparatus used to conduct the freeze-thaw tests. The chamber was contained in a cubical cabinet about 60 cm on an edge. Electric heating and dry-ice cooling were used to change the temperature of the circulating air.

Six thermocouples were used to check on the uniformity of the air temperature within the chamber, and two were mounted on a Portland cement control specimen. Figure 32 shows the Portland cement specimen with an embedded thermocouple used as the temperature control. The external thermocouple was used to show whether there was a significant difference in temperature between the interior and the exterior of the control specimen. The mode of control was on-off, actuated by the embedded thermocouple. In practice there was no more than a 2°C (4°F) temperature difference between the temperature shown by the embedded thermocouple and the external one.

Test Procedure - General - The test procedure was patterned after ASTM C666, Resistance of Concrete to Rapid Freezing and Thawing.[45] Specimens were frozen and thawed in air, which is Procedure B modified in the thawing cycle by using air instead of water immersion to achieve a faster response and, hence, shorter cycle times.

ASTM C-666 involves observing any change in the fundamental transverse frequency of vibration of rectangular prisms on exposure to freeze-thaw conditions. This procedure has the advantage of being a nondestructive test, so one specimen can be used for the entire period of the test. Its disadvantage is that the final results are in terms of a relative dynamic modulus of elasticity, which does not permit prediction of service life under field conditions. Because the specimens to

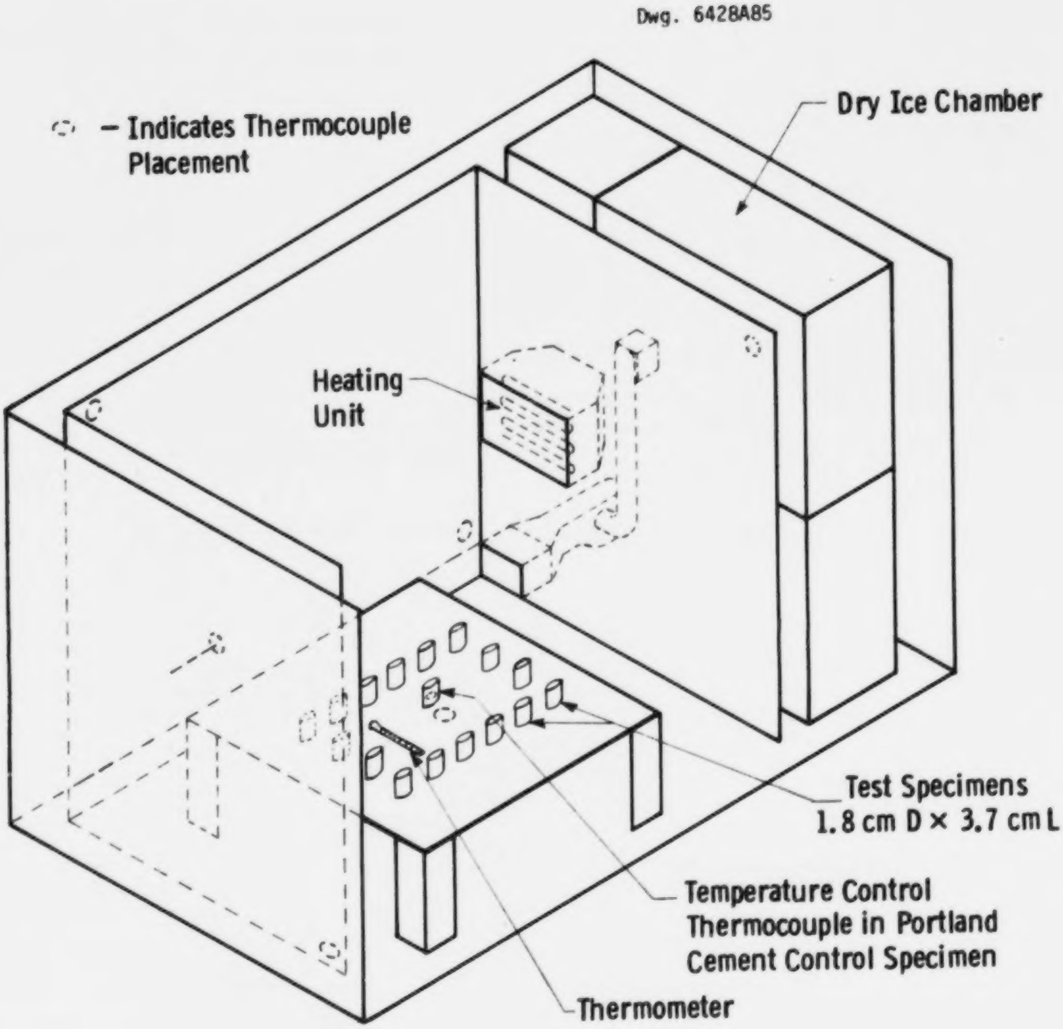

Dwg. 6428A85
◌ – Indicates Thermocouple Placement
Dry Ice Chamber
Heating Unit
Test Specimens 1.8 cm D × 3.7 cm L
Temperature Control Thermocouple in Portland Cement Control Specimen
Thermometer

Figure 30 - Freeze/Thaw Chamber

Dwg. 6428A86

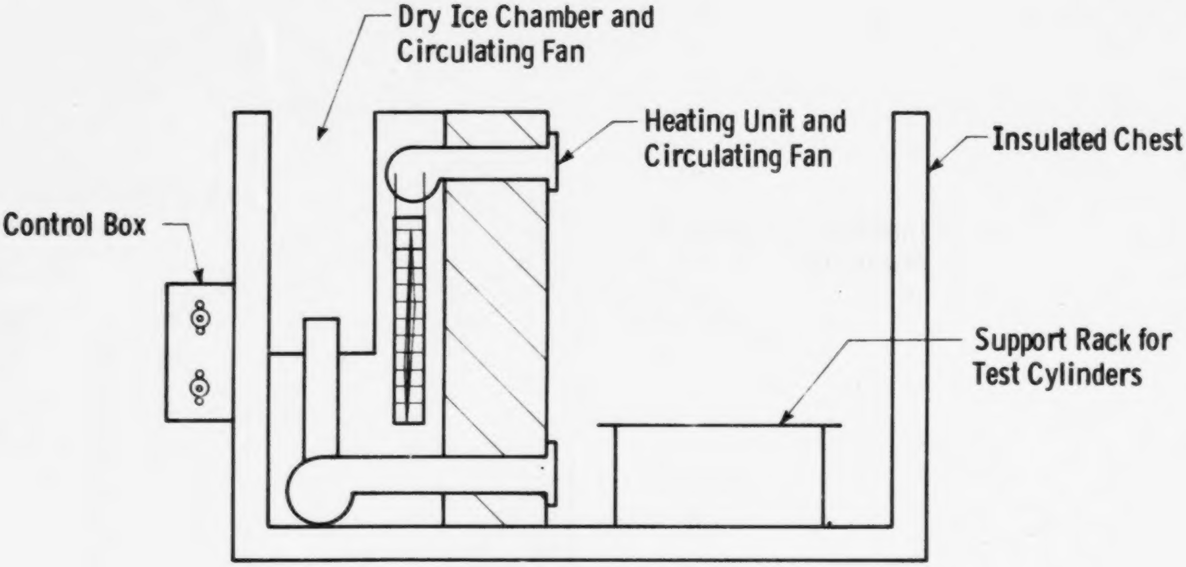

Dry Ice Chamber and Circulating Fan
Heating Unit and Circulating Fan
Insulated Chest
Control Box
Support Rack for Test Cylinders

Figure 31 - Schematic of Freeze/Thaw Chamber

Dwg. 6428A84

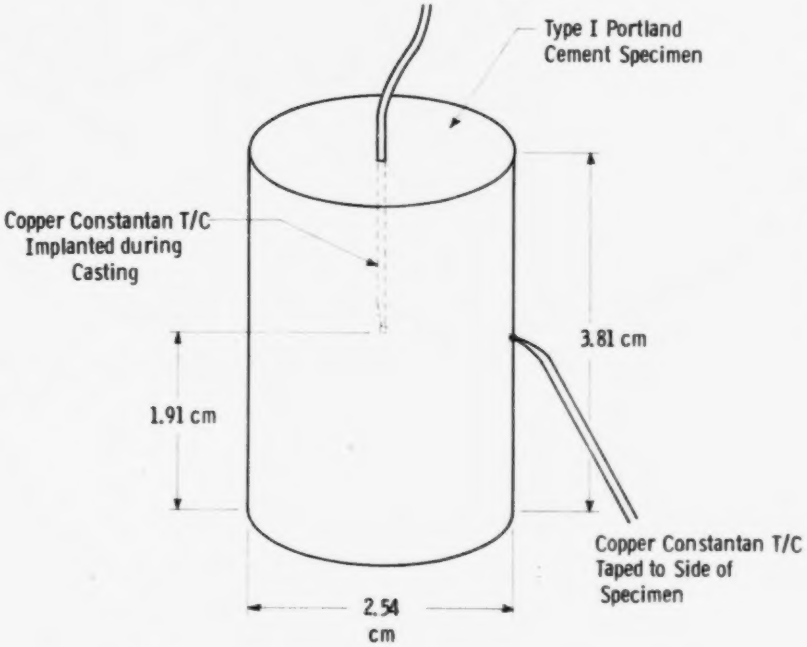

Type I Portland Cement Specimen
Copper Constantan T/C Implanted during Casting
3.81 cm
1.91 cm
Copper Constantan T/C Taped to Side of Specimen
2.54 cm

Figure 32 - Sketch of Type I Portland Cement Control Specimen with Embedded Thermocouple for Temperature Control

be used were small, we decided to use multiple specimens coupled with the direct measurement of compressive strength after various numbers of freeze-thaw cycles. We carried out this procedure by having multiple specimens in the freeze-thaw chamber and removing them in sets after predetermined times of exposure.

Test Matrix

Initially, we planned to obtain data on the effect of spent sorbent source, particle size range, fly ash content, lime content (as reflected in the composition of the spent bed material), and forming method (casting, isostatic pressing, sintering, melting). We would use replicates to estimate experimental random error. The test matrix included three spent bed materials, two mix compositions, two particle size ranges, four cycle times, and three replicates. The number of test samples was therefore 3 x 2 x 2 x 4 x 3, or 144. As noted above, mixes with fly ash were unsuccessful, and time constraints dictated further reduction of the matrix, so only one particle size range was tested, reducing the number of primary test samples of 36.

Table 43 shows the actual test matrix with identifying code numbers for the specimens having the following meaning, using BS0014-3A as an illustration. The first letter denotes the source of the stone:

B	Babcock and Wilcox
E	Exxon
P	Pope, Evans and Robbins.

The second letter denotes the particle size. Two ranges were contemplated: S for small, -63 μm (-230 U.S. sieve), L for large, -125 + 63 μm (-120 +230 U.S. sieve). We tested only the small size. The next two digits denote the weight % fly ash in the mix (zero in all cases tested), and the next two denote the number of days the specimens were cured in water prior to freeze-thaw testing. The next letter denotes N_i, the number of freeze-thaw cycles to which the specimen was

Table 43

TEST MATRIX FOR FREEZE-THAW TESTS ON FBC RESIDUES

	Source of Spent Bed Material		
Number of Cycles	Exxon	B&W	PER
N_1	ES0014A-1/3	BS0014A-1/3	PS0014A-1/3
N_2	ES0014B-1/3	BS0014B-1/3	PS0014B-1/3
N_3	ES0014C-1/3	BS0014C-1/3	PS0014C-1/3
N_4	ES0014D-1/3	BS0014D-1/3	PS0014D-1/3

exposed, and the final digit denotes the number of the replicate. Since the freeze-thaw resistance could not be predicted, the values for A through D were to be selected according to the observed results. We expected that a curve of compressive strength versus time (number of cycles) would be obtained, and it was desirable to distribute the data points selectively along the curve.

Various control specimens were used. To isolate the effect of freeze-thaw cycling, specimens of all three test materials were carried along during the test but outside of the freeze-thaw chamber. Thus, if the outside specimens increased in compressive strength with time, this result would be interpreted as being similar to the normal strength development curve for Portland cement. If freeze-thaw exposure had no effect, then the final values of strength for inside samples would be about the same as those for the outside samples. The initial points on the strength curves would be identical for inside and outside specimens, so only 3 materials x 3 times x 3 replicates, or 27 of these control specimens were needed.

In addition, isostatically pressed samples of Type I Portland cement were used as reference indicators. Again, both inside the outside specimens were used with three points on each strength curve; 9 inside specimens and 6 outside specimens were provided.

As a further exploration of the effect of freeze-thaw cycling on normal materials, specimens were prepared from Portland cement/river sand mixes, using the normal weight ratio of 2.75 parts of sand to 1 part cement. For this effort the number of specimens was the same as for the spent bed materials, 12 inside and 9 outside. The total number of specimens then was 63 primary and control spent bed specimens, 15 primary and control Portland cement specimens, and 21 primary and control cement/sand specimens, or 99 in all.

Test Procedure - Specific - The large number of specimens meant that specimen preparation was spread over a period of time. Enough mix was prepared each time for all replicates required for each planned exposure time. For example, specimen ES0014A, which was to be exposed for N_1 cycles was pressed and cured for 24 hours under water. From it were cut three smaller cylinders to serve as the three replicates for that point on the strength-time curve for Exxon material. These cylinders were cured for thirteen more days in water and then placed in the freeze-thaw chamber. After N_1 cycles of freezing and thawing, they were removed and tested for axial compressive strength. The first set of measurements was made at $N_1 = 0$ cycles, i.e., with no freeze-thaw exposure.

The specimens were observed daily for signs of deterioration (chalking, spalling, cracking, etc.). Because we expected a rapid increase in compressive strength within three days, the second test time (N_2) was set at about 24 hours (12 cycles). The third (N_3) was initially set at twice this number, but since no visible deterioration had occurred it was delayed to 36 cycles. The last test was set at a convenient time after 300 cycles except for one group of B&W samples as noted below. Since the cycles of testing were started at different times, the overall number of cycles of freeze-thaw was 344. Within this time interval the total number of cycles for each material was a convenient arbitrary number greater than 300.

Test Results

Tables 44 through 53 contain the freeze-thaw data on isostatically pressed specimens of spent sorbents from the three FBC pilot plants. The data are plotted in Figures 33 to 37. All the specimens but one survived over 300 cycles of freeze-thaw exposure between the limits -18 and +4°C. One of the B&W samples showed surface spalling at 172 cycles so we determined its compressive strength at that point. Since it was low (22.5 MPa) we checked the other two replicates, but these showed increased strength (79.6 and 73.0 MPa).

In all cases compressive strength increased with exposure to about 50 cycles, after which further increases in strength were smaller. Exposure to freeze-thaw conditions resulted in somewhat higher compressive strengths for Portland cement/river sand, Exxon, and PER specimens and somewhat lower strengths for plain Portland cement and the B&W specimens in comparison to the outside controls which were not exposed to freeze-thaw cycling.

The Portland cement specimen achieved the greatest strengths (90 to 100 MPa, average of three values). The Portland cement/river sand mixtures were in the range of 73 to 83 MPa. Specimens prepared from pilot plant sorbents were in the range of 60 to 83 MPa. These values are above the strength of normal concrete (about 42 MPa).

Since there was no evidence of deterioration in the specimens when the testing was terminated after more than 300 cycles, the technique of compressing the ground spent sorbent and curing it in water appears to offer a way to minimize the environmental impact of the sorbent.

Table 44

FREEZE-THAW RESISTANCE OF ISOSTATICALLY PRESSED CYLINDERS OF FBC SPENT BED MATERIAL FROM B&W PILOT PLANT: TEST SPECIMENS

Sample Designation		Date Pressed	Date Tested	Compressive Strength		Number of Cycles
				MPa	Psi	
BS0014A	1	9/15/77	10/12/77	59.2	8583	0
	2	"	"	45.5	6602	
	3	"	"	19.9	2898	
Average after 0 cycles				41.5	6028	
BS0014B	1	9/15/77	10/13/77	21.1	3060	12
	2	"	"	46.1	6682	
	3	"	"	53.2	7723	
Average after 12 cycles				40.1	5822	
BS0014C	1	9/15/77	10/25/77	44.1	6402	36
	2	"	"	36.4	5278	
	3	"	"	71.9	10430	
Average after 36 cycles				50.8	7370	
BS0014D	1	9/15/77	11/15/77	22.5	3260	172[a]
	2	"	11/8/77	79.6	11550	
	3	"	"	73.0	10590	
Average after 172 cycles				58.4	8467	

[a] Surface spalling observed on Sample 1 but not on 2 and 3.

Table 45

FREEZE-THAW RESISTANCE OF ISOSTATICALLY PRESSED CYLINDERS OF FBC SPENT BED MATERIAL FROM B&W PILOT PLANT: CONTROL SPECIMENS

Sample Designation		Date Pressed	Date Tested	Compressive Strength		Number of Cycles
				MPa	Psi	
OBS0014B	1	9/15/77	10/13/77	68.2	9895	12[a]
	2	"	"	48.8	7080	
	3	"	"	57.6	8351	
Average after 12 cycles				58.2	8442	
OBS0014C	1	9/15/77	10/24/77	34.1	4941	36
	2	"	"	54.5	7897	
	3	"	"	53.2	7713	
Average after 36 cycles				47.3	6850	
OBS0014D	1	9/15/77	12/6/77	79.4	11520	317
	2	"	"	79.4	11510	
	3	"	"	67.0	9720	
Average after 317 cycles				75.3	10917	

[a] This number means these outside controls were tested after a lapse of time corresponding to that for 12 freeze-thaw cycles, so that the effect of aging alone could be compared with the effect of aging and freeze-thaw cycling.

Table 46

FREEZE-THAW RESISTANCE OF ISOSTATICALLY PRESSED CYLINDERS OF FBC SPENT BED MATERIAL FROM EXXON PILOT PLANT: TEST SPECIMENS

Sample Designation		Date Pressed	Date Tested	Compressive Strength		Number of Cycles
				MPa	Psi	
ES0014A	1	9/27/77	10/12/77	25.4	3683	0
	2	"	"	36.5	5299	
	3	"	"	26.6	3865	
Average after 0 cycles				29.5	4282	
ES0014B	1	9/27/77	10/13/77	21.0	3046	12
	2	"	"	41.3	5986	
	3	"	"	16.4	2375	
Average after 12 cycles				26.2	3802	
ES0014C	1	9/27/77	10/24/77	18.1	2626	36
	2	"	"	35.3	5118	
	3	"	"	22.0	3196	
Average after 36 cycles				25.1	3647	
ES0014D	1	9/27/77	12/7/77	76.5	11090	317
	2	"	"	106.9	15504	
	3	"	"	67.7	9820	
Average after 317 cycles				83.7	12140	

Table 47

FREEZE-THAW RESISTANCE OF ISOSTATICALLY PRESSED CYLINDERS OF FBC SPENT BED MATERIAL FROM EXXON PILOT PLANT: CONTROL SPECIMENS

Sample Designation		Date Pressed	Date Tested	Compressive Strength		Number of Cycles
				MPa	Psi	
OES0014B	1	9/15/77	10/13/77	29.1	4224	12[a]
	2	"	"	35.2	5100	
	3	"	"	25.1	3640	
Average after 12 cycles				29.8	4321	
OES0014C	1	9/27/77	10/25/77	48.0	6964	36
	2	"	"	42.2	6118	
	3	"	"	33.5	4854	
Average after 36 cycles				41.2	5979	
OES0014D	1	9/27/77	12/6/77	66.0	9570	317
	2	"	"	43.0	6230	
	3	"	"	61.4	8910	
Average after 317 cycles				56.8	8237	

[a] This number means these outside controls were tested after a lapse of time corresponding to that for 12 freeze-thaw cycles, so that the effect of aging alone could be compared with the effect of aging and freeze-thaw cycling.

Table 48

FREEZE-THAW RESISTANCE OF ISOSTATICALLY PRESSED CYLINDERS OF FBC SPENT BED MATERIAL FROM PER PILOT PLANT: TEST SPECIMENS

Sample Designation		Date Pressed	Date Tested	Compressive Strength		Number of Cycles
				MPa	Psi	
PS0014A	1	9/27/77	10/12/77	29.8	4328	0
	2	"	"	25.7	3729	
	3	"	"	35.7	5172	
Average after 0 cycles				30.4	4410	
PS0014B	1	9/27/77	10/13/77	20.4	2958	12
	2	"	"	37.9	5494	
	3	"	"	30.7	4452	
Average after 12 cycles				29.7	4301	
PS0014C	1	9/27/77	10/24/77	54.4	7886	36
	2	"	"	37.8	5479	
	3	"	"	57.7	8369	
Average after 36 cycles				49.9	7245	
PS0014D	1	9/27/77	12/7/77	80.0	11600	317
	2	"	"	84.5	12260	
	3	"	"	82.9	12020	
Average after 317 cycles				82.5	11960	

Table 49

FREEZE-THAW RESISTANCE OF ISOSTATICALLY PRESSED CYLINDERS OF FBC SPENT BED MATERIAL FROM PER PILOT PLANT: CONTROL SPECIMENS

Sample Designation		Date Pressed	Date Tested	Compressive Strength		Number of Cycles
				MPa	Psi	
OPS0014B	1	9/27/77	10/13/77	27.7	4023	12[a]
	2	"	"	38.2	5539	
	3	"	"	23.3	3377	
Average after 12 cycles				29.7	4313	
OPS0014C	1	9/27/77	10/27/77	52.0	7536	36
	2	"	"	59.3	8598	
	3	"	"	28.2	4086	
Average after 36 cycles				46.5	6740	
OPS0014D	1	9/27/77	12/6/77	66.2	9600	317
	2	"	"	52.8	7660	
	3	"	"	78.9	11440	
Average after 317 cycles				66.0	9567	

[a] This number means these outside controls were tested after a lapse of time corresponding to that for 12 freeze-thaw cycles, so that the effect of aging alone could be compared with the effect of aging and freeze-thaw cycling.

Table 50

FREEZE-THAW RESISTANCE OF ISOSTATICALLY PRESSED CYLINDERS OF TYPE I PORTLAND CEMENT: TEST SPECIMENS

Sample Designation		Date Pressed	Date Tested	Compressive Strength		Number of Cycles
				MPa	Psi	
IP0014A	1	10/3/77	10/24/77	106.9	15504	0
	2	"	"	52.9	7670	
	3	"	"	82.3	11931	
Average				80.7	11702	
IP0014B	1	10/3/77	10/25/77	122.5	17762	12
	2	"	"	83.3	12075	
	3	"	"	48.4	7019	
Average				84.7	12285	
IP0014C	1	10/3/77	12/12/77	77.6	11250	342
	2	"	"	75.8	11000	
	3	"	"	126.9	18400	
Average				93.4	13550	

Table 51

FREEZE-THAW RESISTANCE OF ISOSTATICALLY PRESSED CYLINDERS OF PORTLAND TYPE I CEMENT: CONTROL SPECIMENS

Sample Designation		Date Pressed	Date Tested	Compressive Strength		Number of Cycles
				MPa	Psi	
OP0014B	1	10/3/77	10/25/77	110.9	16086	12[a]
	2	"	"	20.4	2959	
	3	"	"	48.7	7064	
Average after 12 cycles				60.0	8703	
OP0014C	1	10/3/77	12/12/77	104.4	15150	
	2	"	"	65.5	9500	
	3	"	"	135.5	19650	
Average after 343 cycles				101.8	14767	342

[a] This number means these outside controls were tested after a lapse of time corresponding to that for 12 freeze-thaw cycles, so that the effect of aging alone could be compared with the effect of aging and freeze-thaw cycling.

Table 52

FREEZE-THAW RESISTANCE OF CAST CYLINDERS OF PORTLAND TYPE I CEMENT AND RIVER SAND: TEST SPECIMENS

Sample Designation		Date Pressed	Date Tested	Compressive Strength		Number of Cycles
				MPa	Psi	
IPRS14A	1	7/7/77	10/12/77	50.1	7263	0
	2	"	"	25.5	3699	
	3	"	"	30.3	4390	
Average after 0 cycles				35.3	5117	
IPRS14B	1	7/7/77	10/13/77	59.2	8581	12
	2	"	"	47.2	6846	
	3	"	"	44.9	6511	
Average after 12 cycles				50.4	7313	
IPRS14C	1	7/7/77	10/24/77	67.8	9842	36
	2	"	"	67.2	9753	
	3	"	"	49.6	7193	
Average after 36 cycles				61.6	8929	
IPRS14D	1	7/7/77	12/7/77	93.4	13540	317
	2	"	"	92.4	13400	
	3	"	"	60.9	8840	
Average after 317 cycles				82.2	11927	

Table 53

FREEZE-THAW RESISTANCE OF CAST CYLINDERS OF PORTLAND TYPE I CEMENT AND RIVER SAND: CONTROL SPECIMENS

Sample Designation		Date Pressed	Date Tested	Compressive Strength		Number of Cycles
				MPa	Psi	
OPRS14B	1	7/7/77	10/13/77	32.5	4715	12[a]
	2	"	"	52.4	7599	
	3	"	"	30.5	4425	
Average after 12 cycles				38.5	5580	
OPRS14C	1	7/7/77	10/25/77	17.6	2556	36
	2	"	"	35.8	5194	
	3	"	"	47.6	6909	
Average after 36 cycles				33.7	4886	
OPRS14D	1	7/7/77	12/6/77	71.9	10430	317
	2	"	"	79.5	11530	
	3	"	"	74.0	10730	
Average after 317 cycles				75.1	10897	

[a] This number means these outside controls were tested after a lapse of time corresponding to that for 12 freeze-thaw cycles, so that the effect of aging alone could be compared with the effect of aging and freeze-thaw cycling.

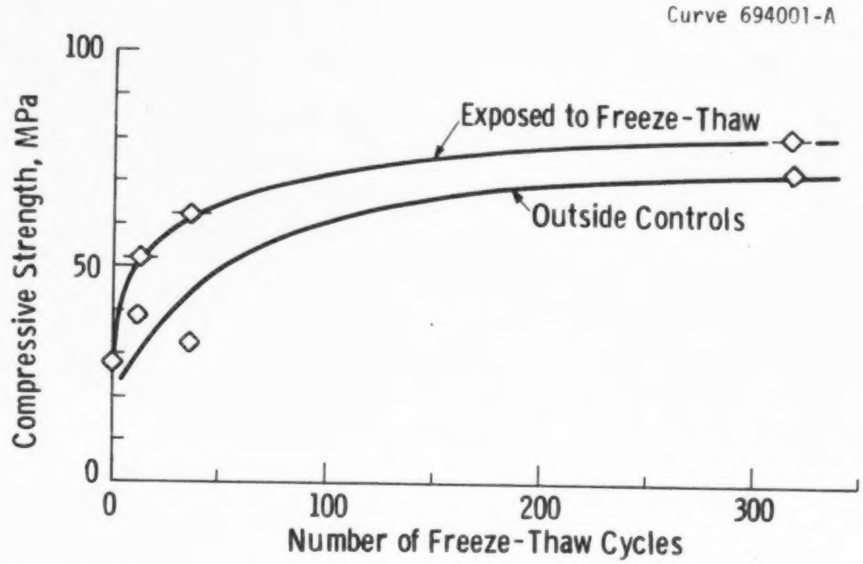


Figure 33 - Freeze-Thaw Resistance of Isostatically Pressed Cylinders of Portland Cement and River Sand

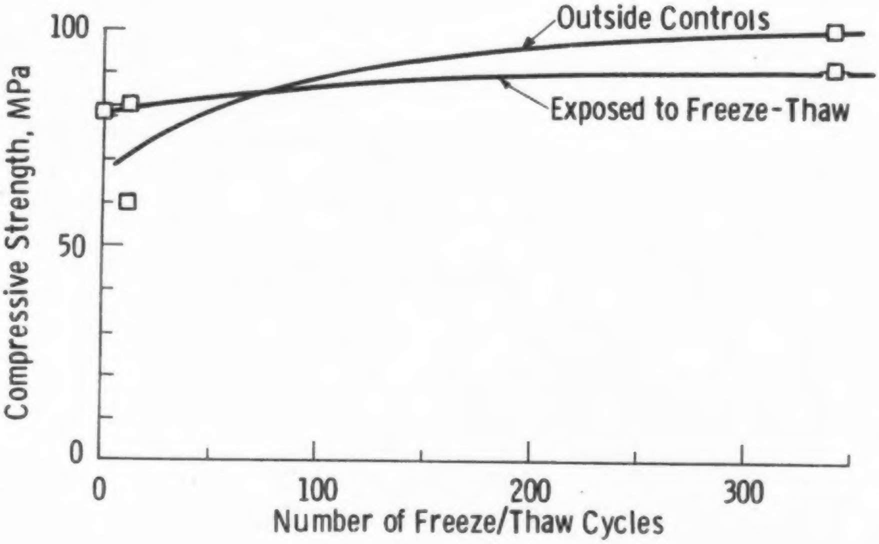


Figure 34 - Freeze-Thaw Resistance of Isostatically Pressed Cylinders of Portland Cement

Curve 693999-A

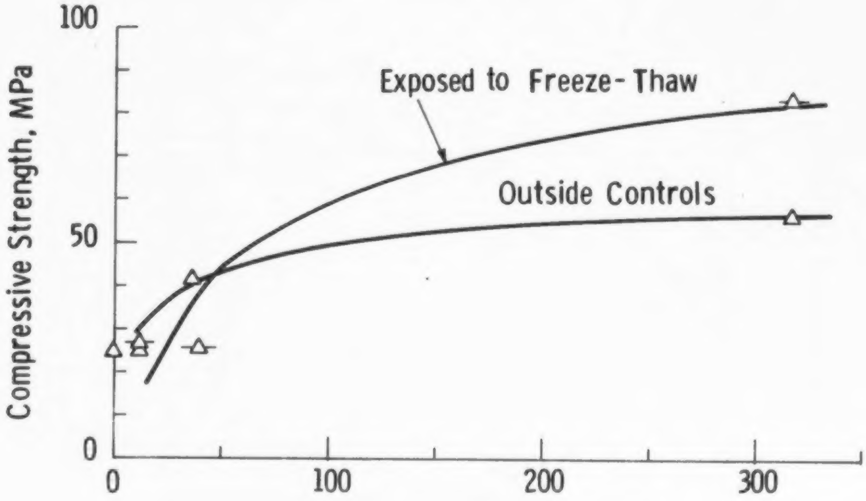


Figure 35 - Freeze-Thaw Resistance of Isostatically Pressed Cylinders of Exxon Spent FBC Bed Material

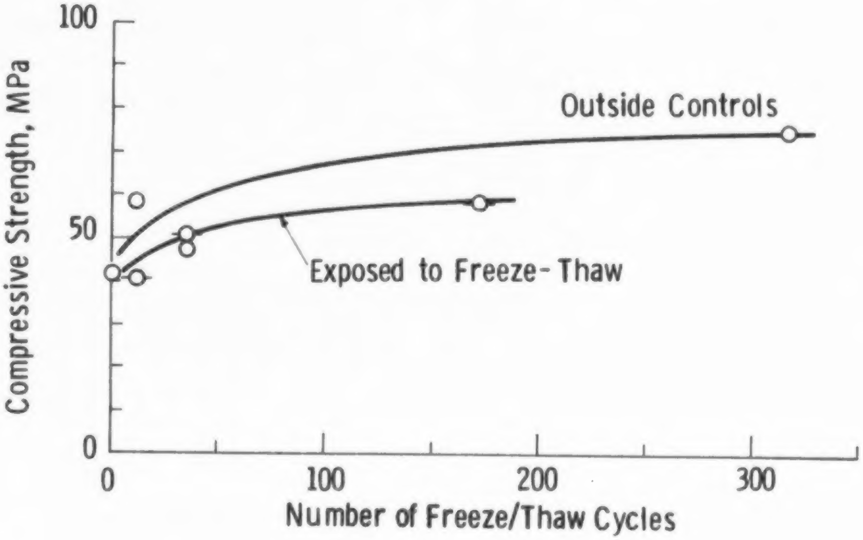


Figure 36 - Freeze-Thaw Resistance of Isostatically Pressed Cylinders of B&W Spent FBC Bed Material

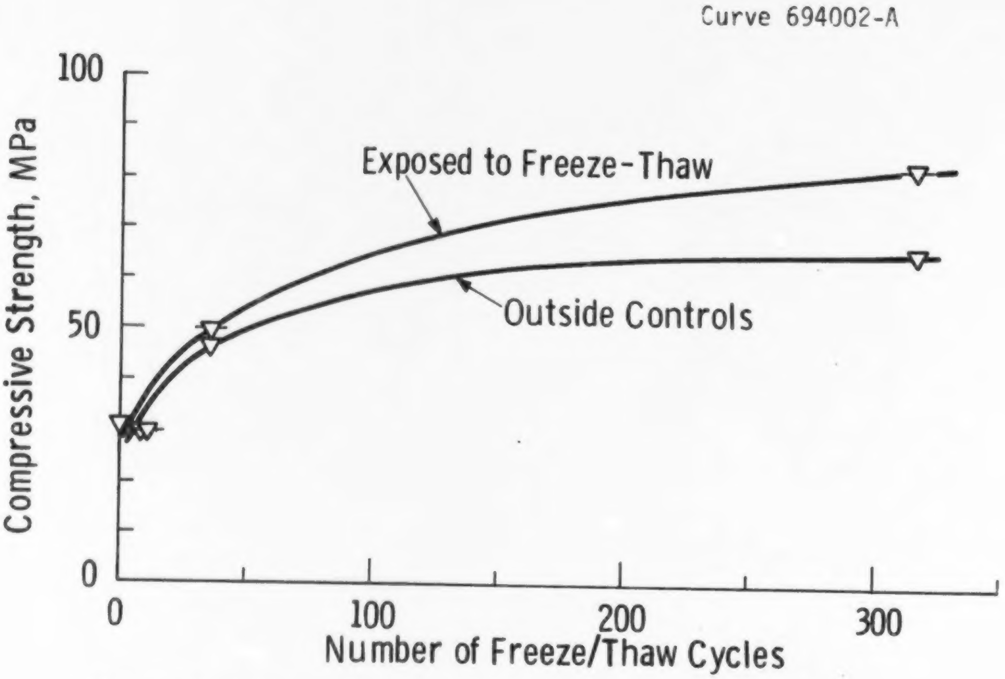
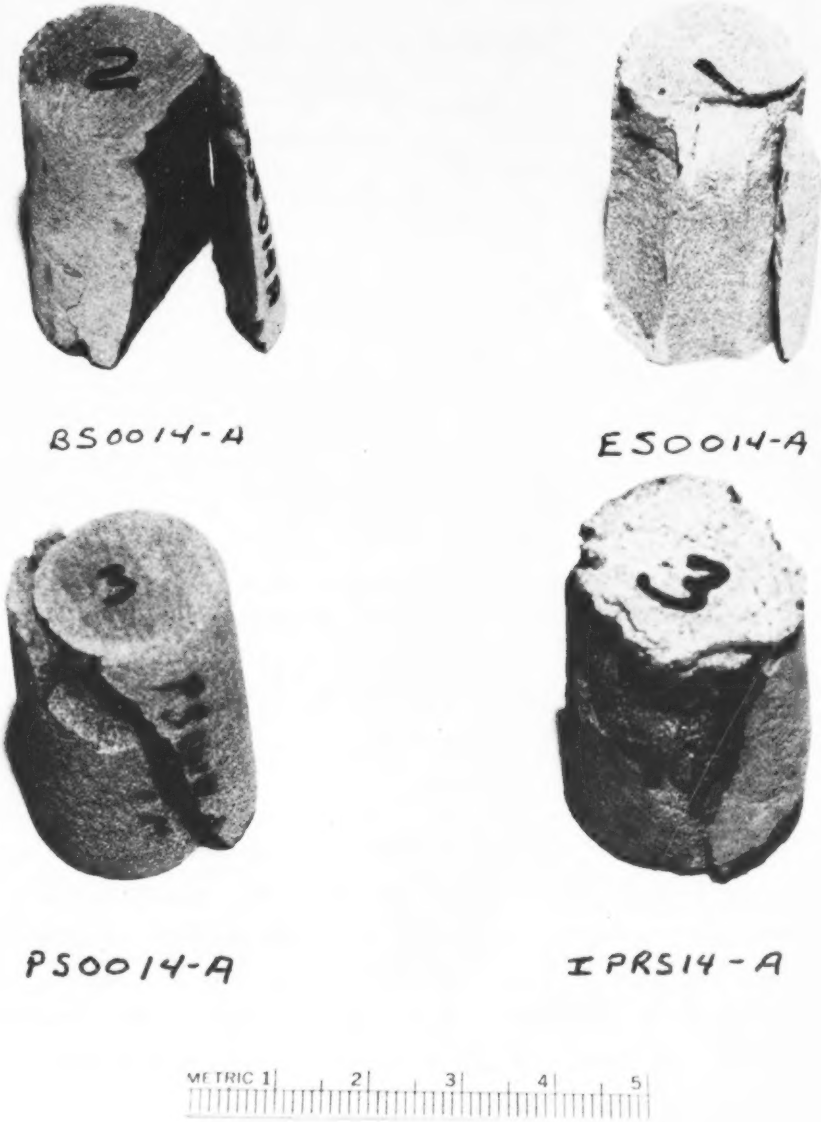


Figure 37 - Freeze-Thaw Resistance of Isostatically Pressed Cylinders of PER Spent FBC Bed Material

These results have prepared the way for future leaching tests on similarly prepared compacts in which the effect of freeze-thaw cycling or leachability will be determined.

Figure 38 shows the mode of failure in compression for the A samples, corresponding to zero freeze-thaw exposure. Of these, the spent bed specimens show cleaner fracture than do the control specimens made with Portland cement and river sand (IPRS14A). The B samples, Figures 39 and 40, after 12 freeze-thaw cycles, however, show similar fractures for spent bed specimens and the cement/sand control specimen both for exposed and unexposed specimens.



BS0014-A

ES0014-A

PS0014-A

IPRS14-A

Figure 38 - Failure Mode of Isostatically Pressed Cylinders of Spent Bed Material in Axial Compression - Initial Specimens

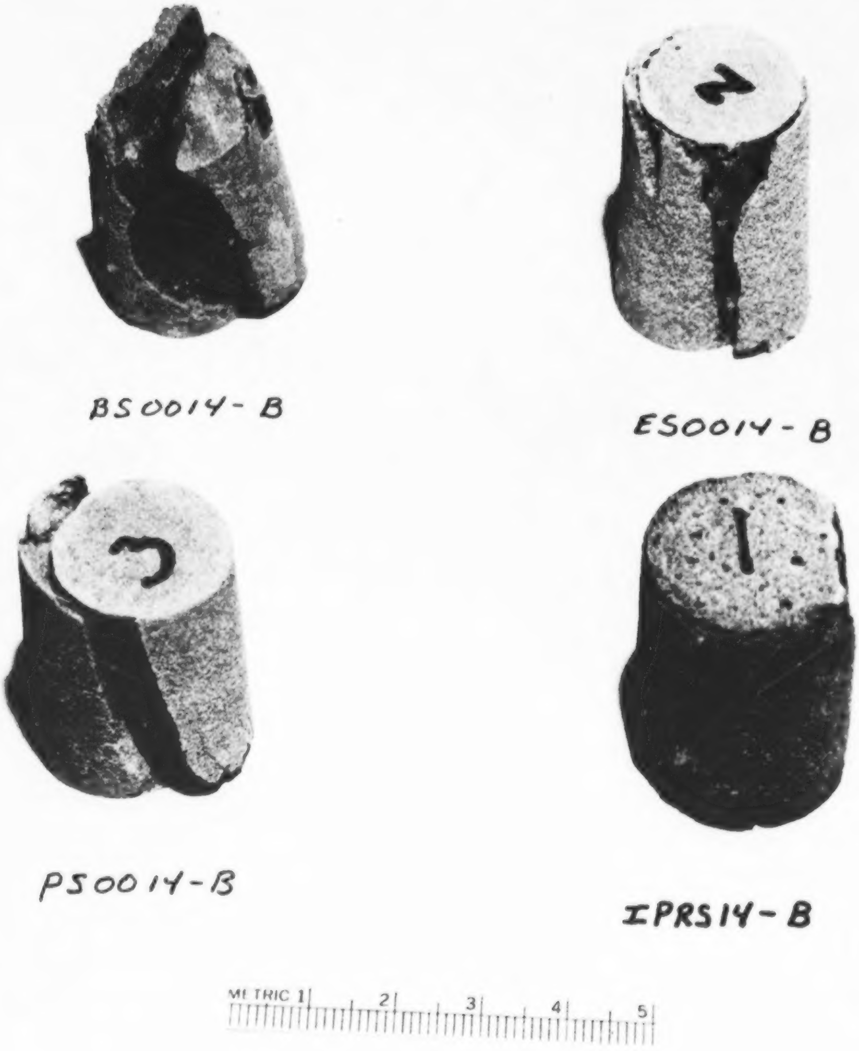
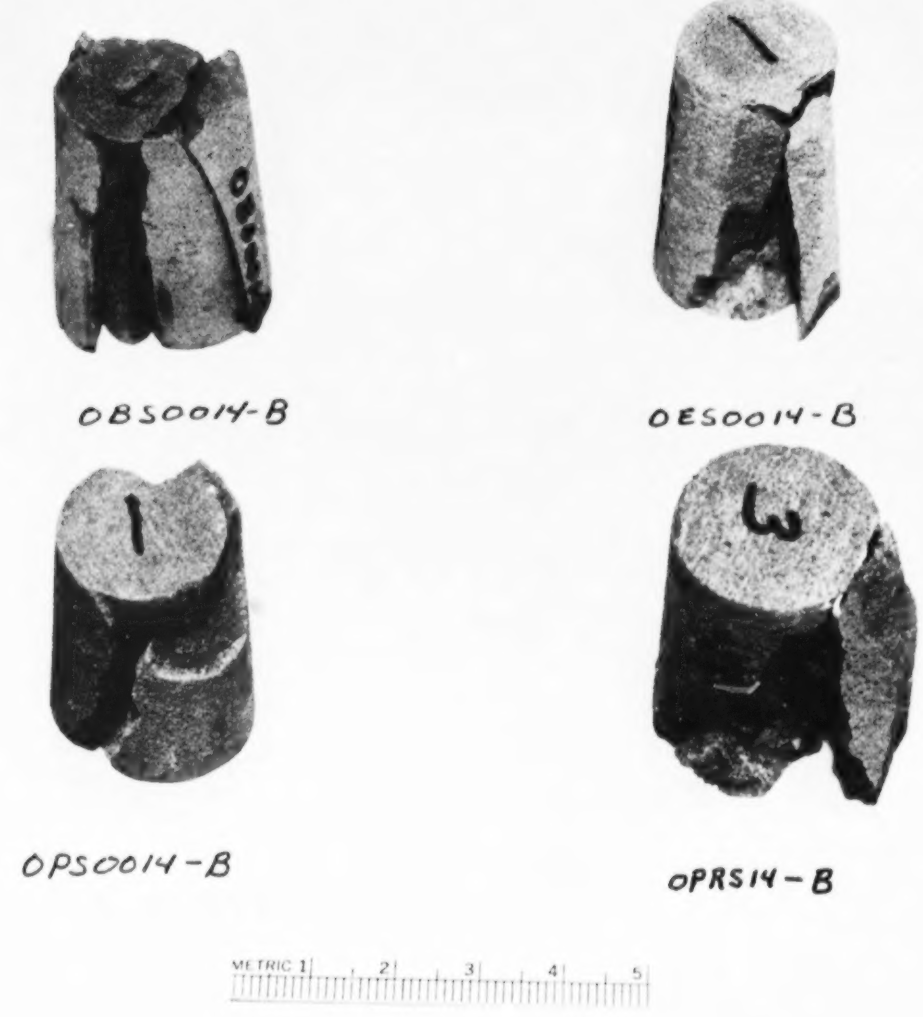

BS0014-B
ES0014-B
PS0014-B
IPRS14-B
METRIC 1 2 3 4 5

Figure 39 - Failure Mode of Isostatically Pressed Cylinders of Spent Bed Material in Axial Compression - After 12 Cycles of Freeze-Thaw Testing


OBS0014-B

OES0014-B

OPS0014-B

OPRS14-B

Figure 40 - Failure Mode of Isostatically Pressed Cylinders of Spent Bed Material in Axial Compression - Outside Controls at Age Corresponding to 12 Cycles of Freeze-Thaw

RM

Tables 54 and 55 show the distributions of cycle times and cycle temperatures during the freezing and thawing portions of the cycles. Cycle temperature, it may be recalled, is the temperature inside one of the Portland cement controls in the freeze-thaw chamber. From these were calculated means and standard deviations for the low point of the freezing portion and the high point of the thawing portion, as recorded in Table 56. Both mean temperatures were slightly higher than in the ASTM C666 procedure. Deviations from the planned temperature limits of -17.8°C and +4.4°C (0° and +40°F) resulted from the simplicity of the equipment plus incidental mechanical difficulties. On two the freezing cycle continued until the temperature had dropped to about -50 to -60°C. The specimens were thus subjected to even more severe stress from freezing than had been planned. The main degradation, however, if any, probably results from cycling through the phase change for water at 0°C.

Table 57 further compares cycle parameters used with those of ASTM. Except for their cooling rates, the parameters are comparable to those for the minimum cycle time of two hours. The maximum cooling rate in the ASTM procedure can be estimated only from the maximum heating rate, since the ASTM does not specify it. The estimated value of 0.4°C/min applicable to the actual tests should be regarded as a minimum maximum. If a lower heating rate is used, less time is available for freezing, and hence the cooling rate must be faster.

A review of the temperature charts showed the temperature changed continuously on both cooling and heating. Only on close examination was it possible to say that a plateau on a time-temperature plot occurred at 0°C, corresponding to the phase change for water. It appears this plateau was of no more than three minutes' duration and was distinguishable only in the early cycles. A simple model of θ_λ, the time required to remove the heat of fusion of water, is given by:

$$\theta\lambda = \frac{a\lambda_f}{(c_s + ac_w)(dt/d\theta)}$$

Table 54

DISTRIBUTION OF CYCLE TIMES

Interval min	Class Mark, min	Number of Cycles in Interval	
		Freezing	Thawing
10-20	15	11	
20-30	25	174	
30-40	35	84	
40-50	45	30	1
50-60	55	14	6
60-70	65	11	78
70-80	75	5	127
80-90	85	3	86
90-100	95	1	24
100-110	105	1	11
110-120	115	2	6
120-130	125	1	
130-140	135		
140-150	145	1	1
170-180	175	1	
220-230	225		1
290-300	295	1	
310-320	315	1	
		341	341
Other[a]		3	3
Total		344	344

---

[a] Recorder out of chart paper.

Table 55

DISTRIBUTION OF CYCLE TEMPERATURES

Interval, min	Class Mark, °F	Number of Cycles in Interval	
		Freezing	Thawing
-14.5 to -9.5	-12.0	1	
-9.5 to -4.5	-7.0	9	
-4.5 to +0.5	-2.0	50	
6.5 to 5.5	+3.0	155	
5.5 to 10.5	8.0	88	
10.5 to 15.5	13.0	29	
15.5 to 20.5	18.0	7	
20.5 to 25.5	23.0		
25.5 to 30.5	28.0		4
30.5 to 35.5	33.0		8
35.5 to 40.5	38.0		68
40.5 to 45.5	43.0		150
45.5 to 50.5	48.0		84
50.5 to 55.5	53.0		24
55.5 to 60.5	58.0		3
-64.5 to -59.5	-62.0	1	
-89.5 to -84.5	-87.0	1	
		341	341
Other[a]		3	3
Total		344	344

---

[a] Recorder out of chart paper.

Table 55

MEAN VALUES FOR CYCLE PARAMETERS

	Mean Value	Standard Deviation	ASTM C666
Freezing			
Temperature, °C	-15.58	4.37	-17.8 ± 1.7
°F	3.95	7.87	0 ± 3
Cycle Time, min	36.4	27.8	
Thawing			
Temperature, °C	6.5	2.8	4.4 ± 1.7
°F	43.7	5.0	40 ± 3
Cycle Time, min	78.5	14.6	30-60 minimum

Table 56

COMPARISON OF SELECTED CYCLE PARAMETERS WITH ASTM C666

	ASTM C666	Actual
Cycle Time		
Total (freezing & thawing)	2-4 hr	114.9 ± 42.4 minutes
Heating time/total time	20% minimum	68%
Rates, °C (°F)/min		
Heating - mean		0.28 (0.51)
maximum	1.57 (2.83)	0.57 (1.02)
Cooling - mean		0.61 (1.10)
maximum	Not specified (est. 0.4 (0.8))	1.23 (2.22)

where

λf = heat of fusion

c_s, c_w = specific heat of solid and water respectively

a = weight fraction of water in the compact and

$dt/d\theta$ = time rate of change of temperature.

For 10 percent water and a cooling rate of 0.5°C/min, about 40 min would be required to remove the heat of fusion. This time indicates that one or more of the following apply:

- The actual water content is no more than about 1 percent.
- The heat of fusion is equilibrated rapidly throughout the compact so that it is removed continuously as sensible heat.
- The total water is distributed throughout the compact so only a very small fraction of it affects the thermocouple tip.

Discussion of Results

The freeze-thaw results on isostatically pressed spent sorbent specimens support the view that spent solids from the fluidized-bed combustion of fossil fuels can be processed to environmentally stable compacts. The reason for the high compressive strengths demonstrated, however, was not evident. In particular, demonstrating the presence of calcium silicates, as in normal Portland cement, would add credibility to the hypothesis that the compacts do have long-term stability. As a first step, we examined the chemical compositions of the test materials, as shown in Table 58.

Here, the oxide compositions for spent bed materials shown in Table 39 were allocated to normal Portland cement constraints, tricalcium silicate, $(CaO)_3 \cdot SiO_2$; dicalcium silicate, $(CaO)_2 \cdot SiO_2$, tricalcium aluminate, $(CaO)_3 \cdot Al_2O_3$; tetracalcium aluminum ferrite, $(CaO)_4 \cdot Al_2O_3 \cdot Fe_2O_3$, and $CaSO_4$. We do not contend that these species exist in the

Table 58

ALLOCATION OF CHEMICAL COMPONENTS IN FBC RESIDUES AMONG NORMAL CEMENT CONSTITUENTS

Constituent	Type I Portland Cement		PER, moles/100 g	Exxon Bed, moles/100 g	B&W, moles/100 g
	Wt %	moles/100 g			
C_3S	46.2	0.202	0.059	0.072	0.037
C_2S	26.2	0.152	0.044	0.054	0.028
C_3A	11.3	0.042	--	--	0.042
C_4AF	8.2	0.017	--	--	0.012
CS'	3.1	0.022	0.249	0.364	0.238
Other	5.0	--			
Excess SiO_2		--	0.350	0.017	
Excess CaO		--	--	--	0.616

Code

C = CaO
S = SiO_2
A = Al_2O_3
S' = SO_3
F = Fe_2O_3

bed materials either as such or in the proportions calculated, but rather that these allocations offer some insight into the nature of the compacts.

We first assumed that all the SO_3 content was tied up as CS' (See Table 58 for coding) for all three residues. Next we found that this left insufficient CaO to form either C_3A from all of the alumina in both the PER and the Exxon spent bed materials or C_4AF from all of the Fe_2O_3 in these residues. Since the average composition of normal Portland cement as shown in Table 58[44] corresponds to 0.202 moles C_3S per 0.152 moles C_2S, the remaining CaO in these two residues was allocated in this proportion, leaving excess free silica as shown. For the B&W residue, the high CaO content permitted showing all of the Fe_2O_3 as

C_4AF, and the balance of the Al_2O_3 as C_3A. The C_3S and C_2S contents were again shown on the mole ratio as above, an amount sufficient to account for all of the silica present, leaving an excess of 0.616 moles CaO per 100 g bed material.

The reason for allocating CaO preferentially to at least C_3S is twofold. First, microscopic studies by others[46] on hydration of these individual components show that C_3S and C_3A start to hydrate immediately, whereas hydration of C_2S requires several days. Hydration appears to result in hydrolysis, releasing $Ca(OH)_2$, some of which may crystallize and some of which may participate in other reactions.

Second, Bogue and Lerch[47] concluded that the early strength Portland cement was due to hydration of C_3S, while the contribution to strength of C_2S was significant only after 28 days, although in one year its strength was about equal to that of C_3S. The contribution of C_3A remained less than 10 percent of that of the C_2S or C_3S.

In comparison to Portland cement, the above allocations suggest that the spent bed materials may contain no more than one-third to one-sixth of the C_3S and C_2S contents of cement. We conclude that these substances are probably not present in amounts sufficient to account for the compressive strengths of the isostatically pressed specimens.

Supplementary Data

X-Ray Inspections

Having demonstrated that isostatically pressed specimens of ground spent material could survive over 300 cycles of freezing and thawing after curing for 14 days under water, further support for the conclusion that these specimens were environmentally stable was sought through X-ray inspections. The objective was to determine whether constituents similar to those in normal concrete, especially hydrated calcium silicates, could be found.

For these inspections samples were taken from the specimens used in the freeze-thaw tests. All specimens had been isostatically pressed dry, cured under water for 14 days, and then aged in ambient air for various lengths of time. The B&W specimen was aged in air for 68 days, the Exxon and the PER specimens for 56 days, and the Portland cement/ river sand reference specimen for 138 days. Before being scanned, all specimens were ground manually in a mortar and pestle to a fine powder estimated to be -44 μm.

Figures 41 to 50 are X-ray diffraction tracings obtained with a Norelco Diffractometer of samples from these ground specimens. Excitation was produced by a current of 35 mA at 40 kV using a copper target with a monochromator. The divergence slit was set at 1° and the receiving slit at 0.2°. The scanning rate was 2 deg/min; the chart speed 1 in/min; the counting rate 500/s.

From these tracings crystal lattice springs can be calculated by the relation $d = 0.770255 \sin \theta$, where θ is one-half the goniometer angle and d is the lattice spacing in Angstroms. The height of the tracings is a measure of the relative intensity of the X-rays exiting from the sample from the various angles of incidence. The ordinate is an arbitrary intensity scale. The instrument is usually set so the highest peak falls near 100 in this scale. If a peak has an intensity greater than 100, it is truncated on the chart, as shown, for example, in Figure 49 for calcined gypsum at a d-spacing of 3.50.

Table 59 shows a comparison of the 20 sharpest peaks and their associated d-spacings as actually observed for calcined gypsum (Figure 49), plaster of paris (Figure 48), gypsum (Figure 47), and silica (Figure 45). The process of concluding that a particular molecular species is present in the sample being analyzed involves the following logic:

1. If a compound is present, its strongest traces ought to be present, and, if absent, these traces should be absent.

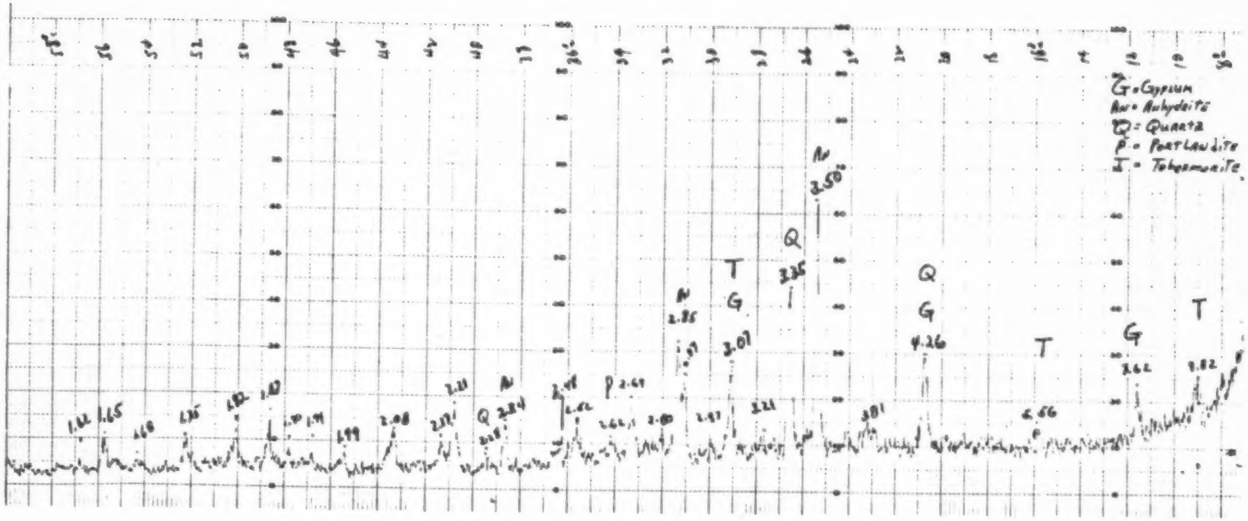


Figure 41 - X-ray Diffraction Tracing from Isostatically Pressed B&W Spent Sorbent

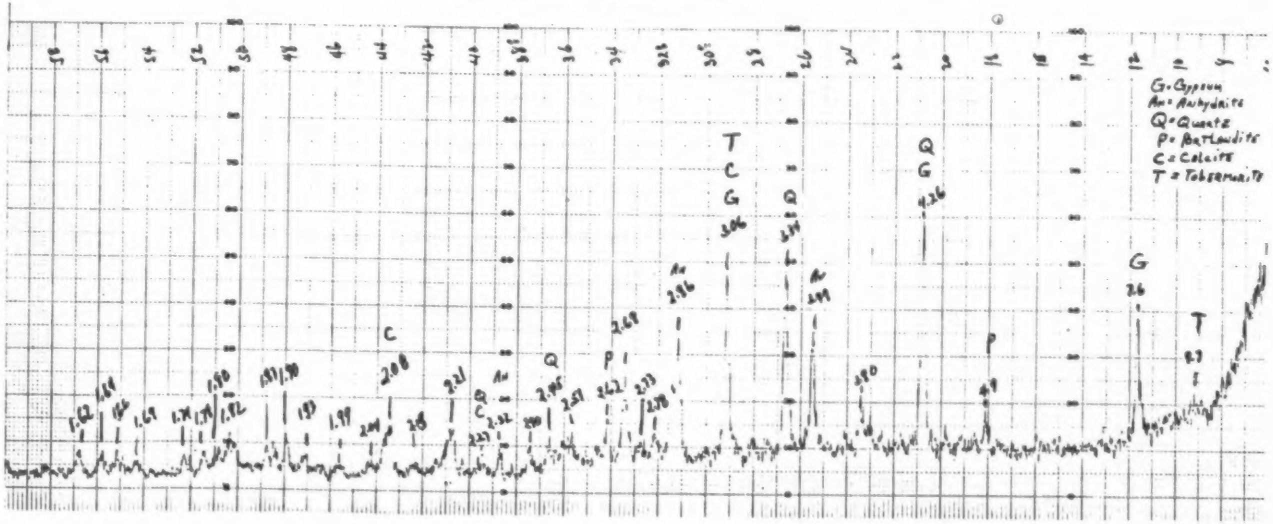


Figure 42 - X-ray Diffraction Tracing from Isostatically Pressed PER Spent Sorbent

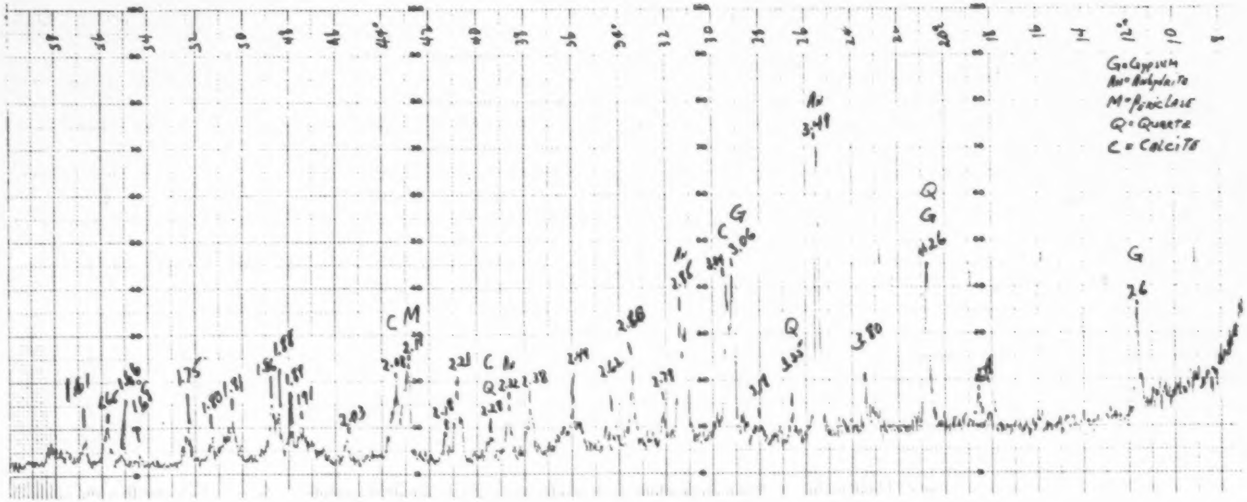


Figure 43 - X-ray Diffraction Tracing from Isostatically Pressed Exxon Spent Sorbent

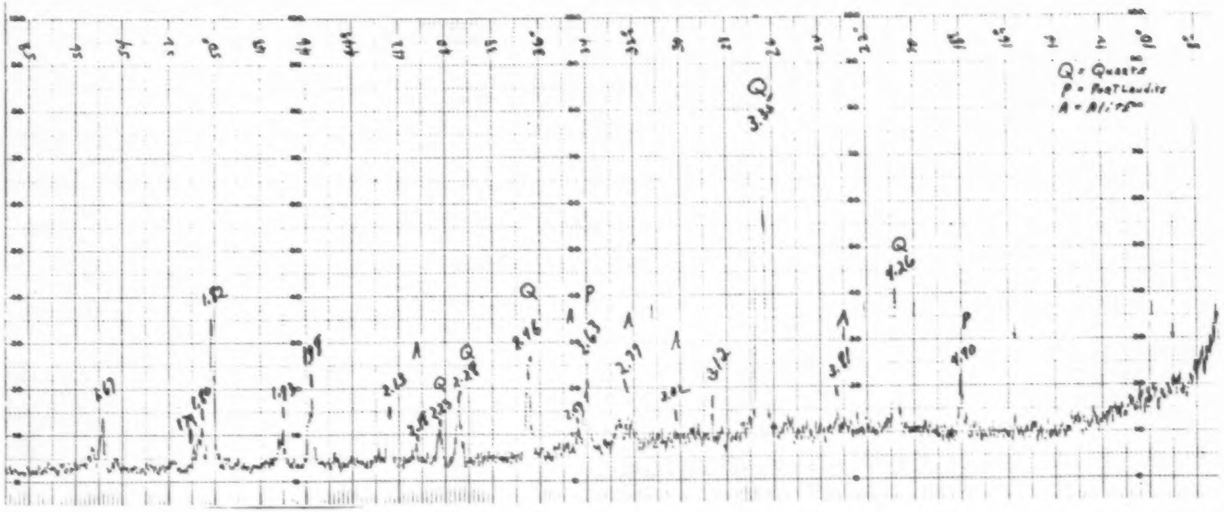


Figure 44 - X-ray Diffraction Tracing from Isostatically Pressed Type I Portland Cement and River Sand

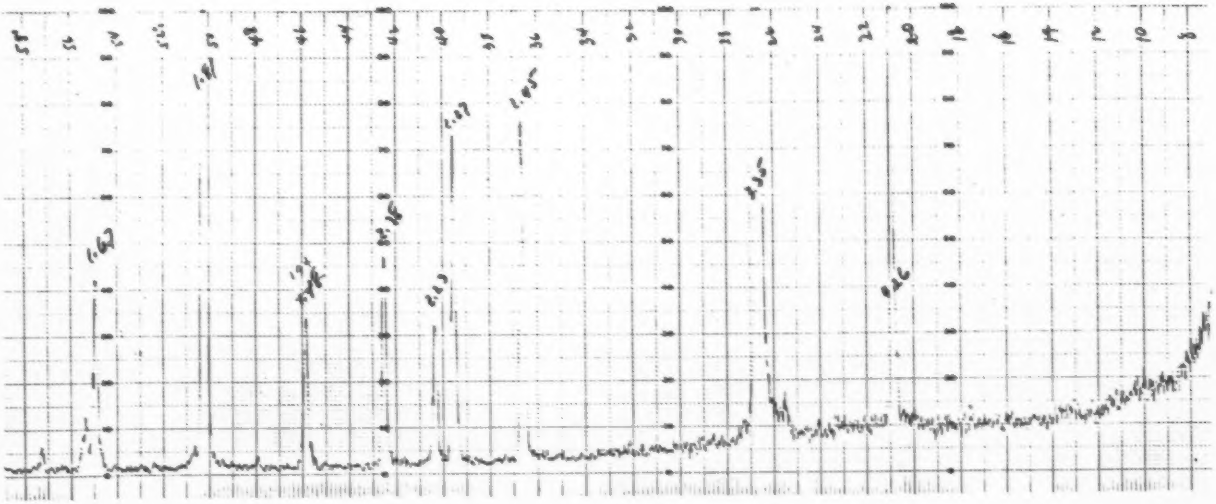


Figure 45 - X-ray Diffraction Tracing from Quartz

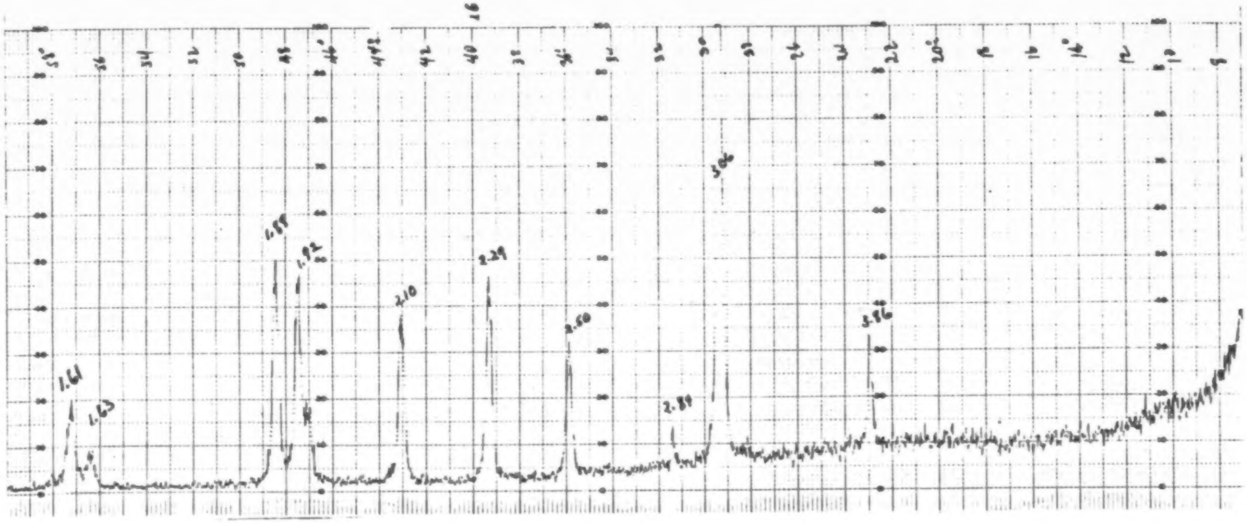


Figure 46 - X-ray Diffraction Tracing from Calcium Carbonate

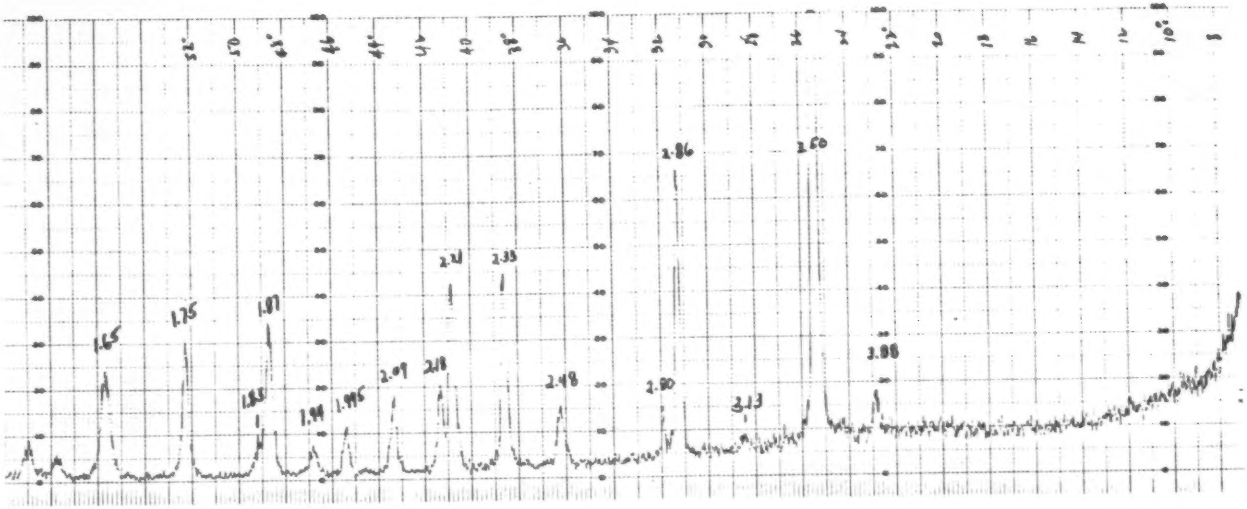


Figure 47 - X-ray Diffraction Tracing from Calcined Gypsum

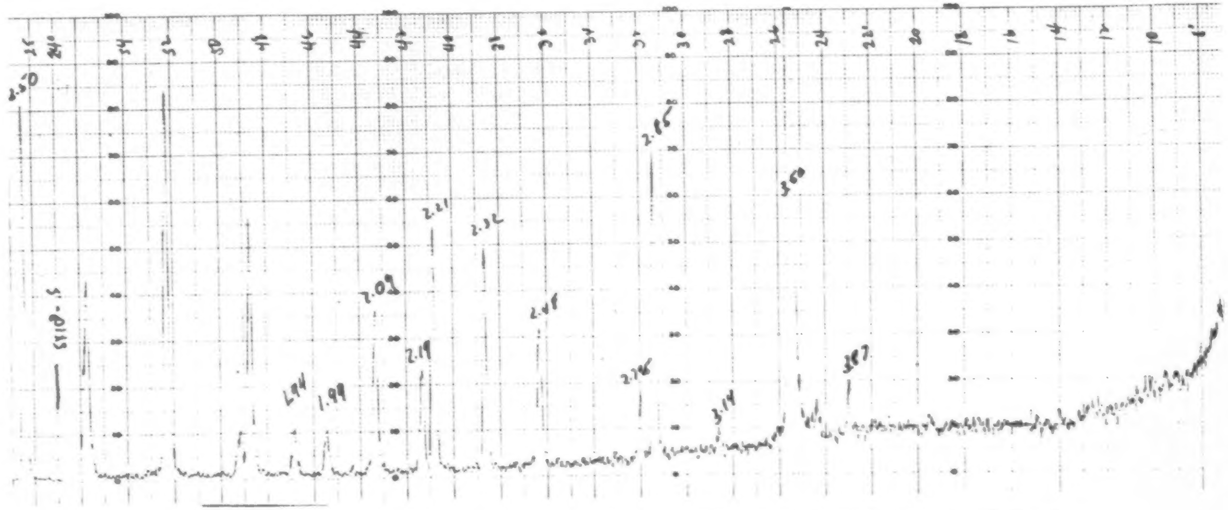


Figure 48 - X-ray Diffraction Tracing from Calcined Plaster of Paris

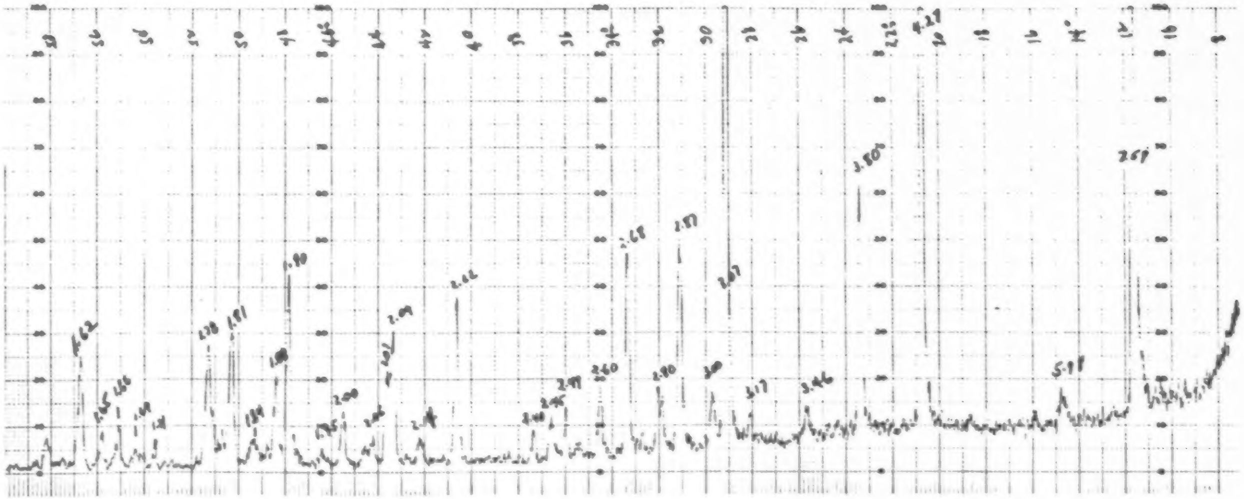


Figure 49 - X-ray Diffraction Tracing from Gypsum

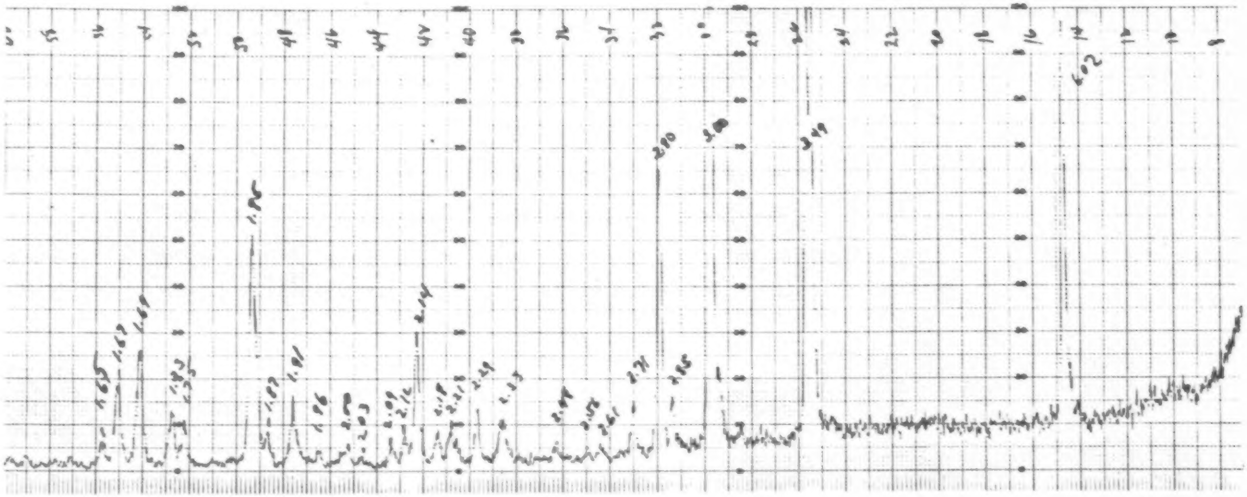


Figure 50 - X-ray Diffraction Tracing from Plaster of Paris

Table 59

COMPARISON OF X-RAY PEAKS FROM SELECTED CALCIUM COMPOUNDS

D, Å	$CaSO_4$	$CaSO_4 \cdot 1/2\ H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCO_3$	SiO_2
8.93			100+	5	
7.56					
4.87				5	
4.57				5	
4.31				5	
4.27			100+		
4.25					100+
4.04				5	
3.88	9				
3.86				24	
3.80			54		
3.50	100+				
3.46		100+			
3.44		100+			
3.34					100+
3.32	5				
3.13	5				
3.06			100+		
3.04				100+	
3.02		17			
3.00		100+	11		
2.87			45		
2.86	63				
2.85		11		8	
2.80	9		14		
2.79		61	13		
2.68			43		
2.60			16		
2.50				30	
2.49			11		
2.48	13				
2.45					73
2.34		9			
2.33	42	9			
2.32		9			
2.29				45	
2.27		11			70
2.24					30
2.22			36		
2.21	41	7			

Table 59 (Continued)

D, Å	$CaSO_4$	$CaSO_4 \cdot 1/2\ H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCO_3$	SiO_2
2.18	19				
2.14		29			
2.12					45
2.10				36	
2.09	16		29	15	
2.07			20		
1.996	10				
1.992			12		
1.979					33
1.932				16	
1.928				18	
1.916				44	
1.910				43	
1.909		15			
1.901			41		
1.894				48	
1.879			19		
1.868	34				
1.850	9				
1.847		50			
1.816					100+
1.812			29		
1.779			26		
1.751		10			
1.748	30	10			
1.732		12			
1.694		25			
1.671					41
1.668		18			
1.665		18			21
1.657					12
1.649	23				
1.633				8	
1.627				8	
1.622			24		
1.609				19	
1.594	5				
1.564	7				
1.540					94
1.527	7				
1.491	11				

2. If the same trace appears for more than one compound, it can be used to identify only one of them.
3. Traces are considered to match references on standards if the d-spacings are within ±0.02 Å.

Thus, if silica in the form of quartz is present, one would expect to find intense traces at d-spacings of 4.25, 3.34, and 1.816 Angstroms. If any of these are absent, quartz is probably not present. Strong traces at d-spacings of 2.45, 2.27, and 1.540 would serve as further confirmation.

Calcium carbonate has only one intense peak - that at 3.04 Angstrom spacing - and so the presence of this molecule depends more heavily on the presence of relatively weak traces - those at 2.29, 1.916, 1.910, and 1.894 Angstroms.

Calcium sulfate can be identified by the strong peak at 3.50 Angstroms and the weaker peaks at 2.86, 2.33, and 2.21 Angstroms.

Gypsum has three strong peaks: 7.56, 4.27, and 3.06 Angstroms. The hemihydrate (plaster of paris) also has three strong peaks: 3.46, 3.44, and 3.00 Angstroms.

Since these characteristic peaks differ by at least 0.02 Angstroms, one would expect that the identification of these five molecular species in a given specimen would be easy; in practice, it was not. First, the intensity of peak is proportional to the concentration of the molecular species. Second, compounds containing similar elements or structures may show peaks at the same d-spacing but at different intensities. Third, the presence of other species may cause the peaks to be displaced somewhat from their normal location on the tracings, corresponding to a modification of the magnitude of the normal d-spacing.

Table 60 is a compilation of all peaks on the X-ray tracing for the B&W specimen for which the relative intensity above background noise was at least 5 percent. The expectation was that the sample would contain at least silica, anhydrite, and possibly hydrated $CaSO_4$. Of the 35 peaks with a relative intensity of 5 or greater, 10 could be assigned to gypsum. Anhydrite could account for another 10 peaks, while silica could account for three more. The hemihydrate of $CaSO_4$ and limestone could not be positively identified from the three peaks that matched their characteristic tracing. This left unidentified nine peaks with relative intensities in the range of 5 to 9 percent. Thus, even if hydrated silicates are present, the intensity of their traces approaches that of background noise.

Tables 61 and 62 are compilations of all the peaks on the X-ray tracings for the Exxon and PER specimens from the freeze-thaw tests for which the relative intensity above background noise was at least 5 percent. The Exxon specimen appears to contain gypsum, anhydrite, silica, and $CaCO_3$, while the hemihydrate of $CaSO_4$ is probably absent. The same result is obtained for the PER specimen. Nine peaks in the Exxon specimen and 21 in the PER specimen remain unidentified.

Table 63 summarizes the conclusions on the constituents expected in the specimens. In only the cement mortar control was it possible to say a calcium silicate was present.

The foregoing detail was presented to stress the uncertainties encountered in attempting to identify molecular species in mixtures of compounds when these compounds have similar d-spacings and therefore show similar peaks. Because a compound may be present in minute amounts, even characteristic peaks may show up with such low intensities as to be indistinguishable from background noise. Natural minerals can be used to produce reference tracings, but differences will appear if samples of a given mineral are taken from different geographic locations. This discrepancy is attributed to the presence of different contaminants.

We reviewed the possibility of matching the peaks via computer. Our X-ray Department had previously attempted this technique but found

Table 60

X-RAY DIFFRACTION PEAKS FROM BABCOCK & WILCOX SPECIMEN NO. OBS0014C-3

Relative Intensity	2θ	d, Å	Relative Intensity above Background	Quartz SiO_2	Anhydrite $CaSO_4$	Plaster of Paris $CaSO_4 \cdot 1/2H_2O$	Gypsum $CaSO_4 \cdot 2H_2O$	Limestone $CaCO_3$
62.5	25.4	3.50	53		3.50	3.46		
44.0	26.6	3.35	35	3.34	3.32 ?			
31.3	31.4	2.85	23		2.86	2.85		2.85
30.0	20.8	4.27	21	4.25			4.27	
27.1	29.1	3.07	19		3.13		3.06	3.04 ?
24.0	31.1	2.87	16				2.87	
17.0	40.8	2.21	13	2.24 ?	2.21	2.21	2.22	
19.1	33.3	2.69	12				2.68	
22.7	11.6	7.62	11				7.56 ?	
13.0	43.3	2.09	11	2.12 ?	2.09		2.09	2.09
14.8	38.7	2.32	10		2.33	2.32		
14.0	48.6	1.872	10		1.868		1.879	
17.0	33.2	2.70	9					
13.9	35.6	2.52	9					2.50 ?
12.8	50.1	1.819	9	1.816			1.812	
25.0	9.0	9.82	8					
12.5	35.5	2.53	7					

Table 60 (Cont'd)

Relative Intensity	2θ	d, Å	Relative Intensity above Background	Quartz SiO_2	Anhydrite $CaSO_4$	Plaster of Paris $CaSO_4 \cdot 1/2H_2O$	Gypsum $CaSO_4 \cdot 2H_2O$	Limestone $CaCO_3$
11.9	36.2	2.48	7	2.45 ?	2.48			
10.0	52.2	1.751	7		1.748	1.751		
10.0	55.7	1.649	7	1.665?	1.649	1.668 ?		
10.0	55.8	1.646	7	(1.657?)		1.665 ?	1.622 ?	(1.633 ?)
15.0	20.5	4.33	6					4.31
14.5	22.9	3.88	6		3.88			3.86
15.0	23.2	3.83	6					
10.5	41.4	2.18	6		2.18			
15.0	15.9	5.57	5					
13.8	23.5	3.78	5				3.80	
13.5	24.1	3.69	5					
13.2	24.2	3.67	5					
12.8	27.7	3.22	5					
12.8	32.0	2.79	5		2.80	2.79	2.79	
11.0	34.2	2.62	5				2.60	
10.5	36.0	2.49	5				2.49	
8.1	39.5	2.28	5	2.27		2.27		2.29
7.8	45.4	1.996	5		1.996		(1.992 ?)	

Table 61

X-RAY DIFFRACTION PEAKS FROM EXXON SPECIMEN NO. OES0014C-3

Relative Intensity	2θ	d, Å	Relative Intensity above Background	SiO_2	$CaSO_4$	$CaSO_4 \cdot 1/2H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCO_3$
70.9	25.5	3.49	64		3.50			
43.0	29.2	3.06	36				3.06	
43.8	20.7	4.29	34				4.27	4.31 ?
40.8	29.4	3.04	34					3.04
33.0	31.4	2.85	26			2.85		2.85
31.5	31.2	2.86	25		2.86			
35.5	11.6	7.62	22				7.56	
25.0	42.9	2.11	22	2.12				
23.0	43.0	2.10	20		2.09		2.09	2.10, 2.09
22.8	33.4	2.68	17				2.68	
20.0	43.4	2.08	17		2.09		2.09, 2.07	2.09
18.0	40.9	2.20	15		2.21, 2.18	2.21	2.22	
15.0	48.7	1.868	12		1.868			
15.1	38.7	2.32	11		2.33	2.33, 2.32		
19.0	23.4	3.80	10				3.80	
14.1	37.8	2.38	10					
13.2	48.4	1.879	10				1.879	
14.0	36.0	2.49	9				2.49	
11.8	50.4	1.809	9				1.812 ?	
11.0	55.7	1.649	9		1.649			
17.0	18.6	4.77	8					
10.9	47.5	1.912	8		1.748	1.748		1.910
10.3	52.3	1.748	8					
16.1	17.9	4.95	7					
13.2	26.6	3.35	7	3.34				

Table 61 (Cont'd)

Relative Intensity	2θ	d, Å	Relative Intensity above Background	SiO_2	$CaSO_4$	$CaSO_4 \cdot 1/2H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCO_3$
13.5	32.1	2.79	7			2.79	2.79	
10.0	47.4	1.916	7					1.916
18.5	9.9	8.93	6					8.93
19.9	10.4	8.50	6					
20.0	10.7	8.26	6					
13.7	28.7	3.11	6		3.13 ?			
13.0	29.8	3.00	6			3.00	3.00	
22.2	9.3	9.50	5					
13.6	15.8	5.60	5					
13.2	16.0	5.53	5					
14.7	23.1	3.85	5					3.86
14.8	23.3	3.81	5				3.80	
10.6	34.5	2.60	5				2.60	

Table 62

X-RAY DIFFRACTION PEAKS FROM PER SPECIMEN NO. OPS0014C-3

Relative Intensity	2θ	d, Å	Relative Intensity above Background	SiO_2	$CaSO_4$	$CaSO_4 \cdot 1/2\ 2H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCO_3$
60.0	20.8	4.27	51	4.25 ?			4.27	3.04 ?
47.1	29.2	3.06	40				3.06	
48.2	26.7	3.34	38	3.34	3.32 ?			
38.8	11.7	7.56	26				7.56	
33.7	31.2	2.86	26		2.86	2.85	2.87	2.85
35.1	25.5	3.49	25		3.50			
25.0	31.1	2.87	17		2.86	2.85	2.87	2.85
25.0	33.4	2.68	17				2.68	
23.8	31.4	2.85	16			2.85		2.85
25.0	11.6	7.62	12					
21.8	23.8	3.80	12				3.80	
14.0	40.7	2.22	11				2.22	
14.1	43.4	2.08	11		2.09		2.09, 2.07	2.09
16.0	34.2	2.62	10				2.60	
13.4	40.9	2.20	10		2.21, 2.18	2.21	2.22	
18.9	18.1	4.90	9					4.87
12.1	47.9	1.897	8					1.894
10.3	50.3	1.812	8				1.812	
16.0	18.0	4.92	7					
12.4	36.6	2.45	7	2.45				
10.0	37.4	2.40	7					
9.8	38.7	2.32	7		2.33	2.32, 2.33		
15.9	13.1	6.75	6					
15.0	17.9	4.95	6					
15.2	19.8	4.48	6					

Table 62 (Cont'd)

Relative Intensity	2θ	d, Å	Relative Intensity above Background	SiO_2	$CaSO_4$	$CaSO_4 \cdot 1/2\ 2H_2O$	$CaSO_4 \cdot 2H_2O$	$CaCO_3$
14.8	22.5	3.95	6					
19.4	23.3	3.81	6				3.80	
14.4	24.1	3.69	6					
12.8	28.1	3.17	6					
13.0	32.2	2.78	6		2.80	2.79	2.80, 2.79	
13.8	35.7	2.51	6					2.50
8.0	45.6	1.988	6				1.992	
10.9	48.5	1.875	6				1.879	
8.2	55.8	1.646	6		1.649			
8.3	56.7	1.622	6				1.622	
26.1	8.0	11.04	5					
22.8	9.2	9.60	5					
13.7	16.0	5.53	5					
14.0	18.6	4.77	5					
13.8	19.1	4.64	5					
14.4	20.4	4.53	5					
13.8	21.7	4.09	5					
12.2	27.7	3.22	5					
12.0	32.6	2.74	5					
8.2	39.5	2.28	5	2.27		2.27		2.29
9.8	48.8	1.865	5		1.868			
9.8	50.8	1.796	5					
9.8	51.0	1.789	5					
8.0	51.5	1.773	5					
7.8	52.3	1.748	5		1.748	1.748		
8.3	55.2	1.622	5	1.665		1.665		

Table 63

X-RAY DIFFRACTION ANALYSIS OF SELECTED ISOSTATICALLY PRESSED SPECIMENS OF FBC RESIDUES AFTER 14 DAYS CURING IN WATER

Constituents	Sample Number			
	Cement Mortar OPRS14C-3	Babcock & Wilcox OBS0014C-3	Exxon OES0014C-3	Pope, Evans & Robbins OPS0014C-3
$Ca(OH)_2$	Minor	Trace	ND[a]	Trace
$CaSO_4$	Trace	Major	Major	Minor
$CaSO_4 \cdot 2H_2O$	Trace	Major	Major	Major
$CaSO_4 \cdot 1/2H_2O$	---	NC[b]	NC	NC
MgO	---	---	Minor	---
SiO_2	Major	Minor	Trace	Minor
$CaSiO_3$	Trace	ND	ND	ND
$CaCO_3$	---	NC	Trace	Trace

[a] ND = Not detected
[b] NC = Not confirmed

that the results were variable. If the tolerance on the d-spacing was set too wide, the number of compounds containing a particular peak was increased; if set too narrow, a possible identification would be missed. We concluded that some other technique was needed. One such possibility, although not attempted here, is a microscopic technique that might take into account crystal form and index of refraction. The latter would depend on the preparation of thin sections. The overall objective of this line of investigation would be to make more definite predictions about the long-term environmental stability of the solid compacts.

Weight Loss on Heating

Two specimens were spot checked by TGA for their weight loss when heated to 1000°C as another means of determining whether hydrated silicates could be present.

Table 64

WEIGHT LOSS FROM CURED ISOSTATICALLY PRESSED SPECIMENS OF FBC RESIDUES WHEN HEATED TO 1000°C

Sample	% Loss @ 700°C	% Loss @ 1000°C
IP0014C-3	9.93	10.82
ES0014C-3	12.00	13.70

The weight losses to 700° interpreted as water losses are only about half the theoretical values for hydration of Portland cement (about 24 wt %). It is interesting that compressive strengths well above those of normal cement can be obtained with so little water.

Discussion

The low water-content of the cured, isostatically pressed specimens does not support the conclusion that the high compressive strengths obtained are due to the presence of hydrates typical of Portland cement.

The only hydrate identified, gypsum, is reported in the literature to have a compressive strength in the range 6.2-1512 MPa (900-2200 psi). An alternative explanation is that the strength is due to intermolecular forces operative because of the fine particle size of the powders prior to being pressed and to the high pressure used to form the specimens.

This explanation would be consistent with the freeze-thaw results in that any ice crystals formed during the freezing portion of the cycle would have unoccupied pore volume into which to expand. If the pores were saturated with water, the specimens would probably have deteriorated in the freeze-thaw testing. Hence, formation of compacts by dry pressing of FBC residues ground to at least 100 percent through 63 μm with subsequent water curing for 14 days offers promise of a way to reduce the potential for leachate production from these residues that at the same time confers long-term freeze-thaw resistance on the compacts.

Aggregate

Process

Two of the processes conceived for disposing of FBC residue lead to its utilization as aggregate. The compacts described in the section under Pressed Material were investigated with the view of depositing them in the environment, but they might also be usable as coarse aggregate. Another possibility is to take the granular material from the FBC process and use it directly as fine aggregate in concrete. We therefore devised tests to explore the technical feasibility of this option.

Concrete is basically a physical mixture of three types of solids. Most of the volume of this mixture consists of fragments of rock of size distributions appropriate to the application. This is termed coarse aggregate. The aggregate is held together by cement, which develops its binding strength when water is added to it through the formation of hydrated silicates. To minimize the quantity of cement required in the mixture, the voids between the coarse aggregate pieces are filled with fine aggregate, which typically is a sand. Sand also is a source of additional silica which can react with $Ca(OH)_2$ released on hydrolysis of silicates in the cement to form gels.

Test Materials

Sintered pelletized fly ash (SFA), 1/2 in. x No. 8, from the Penn Virginia Materials Corporation of Eastlake, Ohio was used as the coarse aggregate. Chemical analysis of typical Penn Virginia SFA is in Table 65. Chemical analysis for FBC residues were shown in Table 40.

Bulk density measurements of spent sorbents and various fly ashes are in Table 66. Although the as-is material was used in the tests described below, the bulk densities of two fractions are included for future reference.

Table 65

TYPICAL ANALYSIS OF PENN VIRGINIA SINTERED FLY ASH

Constituent	Weight %, Dry Basis
SiO_2	53.4
Al_2O_3	27.8
Fe_2O_3	15.2
CaO	2.52
MgO	0.48
SO_3	0.04
C	2.25
LOI	1.91
Available alkalis	0.13

Note

1. Moisture content of as-is sample: 5.52%

Table 66

BULK DENSITY OF MATERIALS FOR AGGREGATE TESTS, g/cc

Material	As is	-125 + 44 μm	-44 μm
FBC Residues			
B&W-Run 19	1.084	1.236	0.996
PER	1.513	1.448	1.252
Exxon-Run 43-3	1.587	1.511	1.245
Fly Ashes from Conventional Boilers			
Duquesne	1.099		
Wyoming	1.413		
Penn Virginia SFA	1.450		

As a preliminary, water absorption measurements were made on 100-g random samples of Penn Virginia 1/2 in. x No. 8 SFA. The SFA appeared porous and therefore potentially capable of absorbing a significant portion of the water added to the mix, thereby interfering with the desired hydration reactions. Three immersion times of duplicate samples were investigated. The first 100 g samples were taken directly from the 208 ℓ (55 gal) drum of the as-received Penn Virginia fly ash and dried to constant weight at 105°C. The weight loss was then calculated as percent moisture. Two duplicate samples, labelled A and B, were immersed in water for 24 and 144 hours, respectively. The samples were blotted dry with paper towels, weighed, and then oven dried to constant weight at 105°C. The results are presented in Table 66. The samples appear to show negligible changes in water content when exposed for 24 hours and no change thereafter. One gram of aggregate takes on about 0.017 cc additional water in 24 hours. This may be a significant change when compared to the total pore volume of the dry aggregate in investigation of freeze-thaw resistance but is considered unimportant in the explanation of behavior in hydration reactions.

Performance Characteristics

Proceeding, then, with the main tests, we found that mixes of B&W, PER, and Exxon spent bed materials, 1/2 in. by No. 8 SFA, Type I Portland cement and water developed enough heat to produce steam and premature set of 7.6 cm by 15.2 cm (3 in. by 6 in.) cylindrical specimens. Slaking the spent bed materials prior to blending eliminated the problems caused by heat generation. A 500 g sample of each was therefore hydrated with 1000 ml of water, mixed thoroughly, and allowed to cool to room temperature. The excess water was decanted and saved for addition later.

The specimens were made using a modified ASTM C-192 procedure for mortar composition, substituting 1/2 in. by No. 8 SFA and sorbent for white Ottawa sand.

The final mortar compositions consisted of 500 g of Portland Type I cement, the slaked stone prepared as described above, 500 g of 1/2 in. by No. 8 SFA, and the previously decanted water of hydration. One specimen was prepared with this composition for each of the three FBC spent bed materials. In the case of the B&W material, an additional specimen, BA 8527, was prepared using a lower bed material/SFA ratio (150 g of bed material/850 g SFA). The casting procedure was as per ASTM C192 using 7.6 cm by 15 cm (3 in. by 6.2 in.) cardboard cylinder molds. A control cylinder of Type I Portland cement and white Ottawa sand was also cast. All of the specimens were moist cured for a 14-day period except for BA 8527, which was moist cured for 27 days The specimens were then tested for axial compressive strength, with the results as shown in Table 67. The data show that the Exxon and PER spent bed materials, after preslaking, can be used as fine aggregate in conjunction with SFA to make Portland cement mortars that develop compressive strengths equal to normal concrete at the same curing age. Both the B&W specimens were substantially lower in strength (less than half). One possible reason is the higher CaO content, which may have resulted in excessive $Ca(OH)_2$

Table 67

WATER ABSORPTION BY PENN VIRGINIA 1/2 IN. X NO. 8 SINTERED PELLETIZED FLY ASH

Immersion Time, hr	Weight % Moisture	
	Sample A	Sample B
0	3.0	3.4
24	4.7	5.2
144	4.7	5.3

Notes:

1. Samples were random 100 g portions from 208 ℓ (55 gal) drum.
2. Samples were blotted dry with paper towels after immersion and then oven dried to constant weight at 105°C.

Table 68

COMPRESSIVE STRENGTH OF CYLINDERS MADE FROM PORTLAND CEMENT, FBC SPENT BED MATERIALS AND SINTERED FLY ASH

Specimen Designation	Spent Sorbent	Axial Compressive Strength, 14 days	
		MPa	Psi
BA 5014	B&W Run 19	10.1	1460
BA 8527	B&W Run 19	10.7	1550
EA 5014	Exxon Run 43	22.9	3320
PA 5014	PER	22.1	3210
PWS 14 (2)	None	23.8	3450

Notes:

1. Cylinder size 7.62 cm D by 15.24 cm H (3 in. by 6 in.).
2. Portland cement/white sand control.

content in the final cylinders. The BA 8527 specimens, however, which had less than one third as much bed material as did BA 5014, showed only a slight increase in strength relative to BA 5014. Further tests are clearly needed to identify the reason for this behavior.

ENVIRONMENTAL IMPACT OF PROCESSED WASTE

Empirical Correlation for Laboratory Results

Further perspective on the effect of fixation on potential environmental impact is provided by analysis of selected data from Section 6 covering the leaching behavior of raw and processed residues from Run 27 of the Exxon miniplant. The data on intermittent leaching could be used to calculate the average rates of extraction of a particular solute, as calcium, for each time period. We chose rather to calculate the amount of calcium leached in terms of mg-moles/extraction, cumulate these values, and plot these totals against the number of the extraction period. These data would simulate repeated rainfalls on exposed residues, either fixed or as produced, if we assume a constant rainfall/solid weight ratio and 100 percent efficiency of contacting.

The data are presented on a normalized basis in Figure 52, obtained by dividing each of the ordinate values of Figure 51 by the weight of the specimen involved. Figure 52 shows the substantial reduction in leaching obtained by fixation [Samples I1D and I14D' versus spent bed material (SBM)]. It also shows that crushing the cubes results in material from which more calcium can be leached than from the raw residue.

We noted that these curves developed constant slopes after about 10 extractions, so empirical equations of the following form were fitted to the data:

$$L_T = L_0(1 - e^{-b_1 N}) + b_2 N \quad ,$$

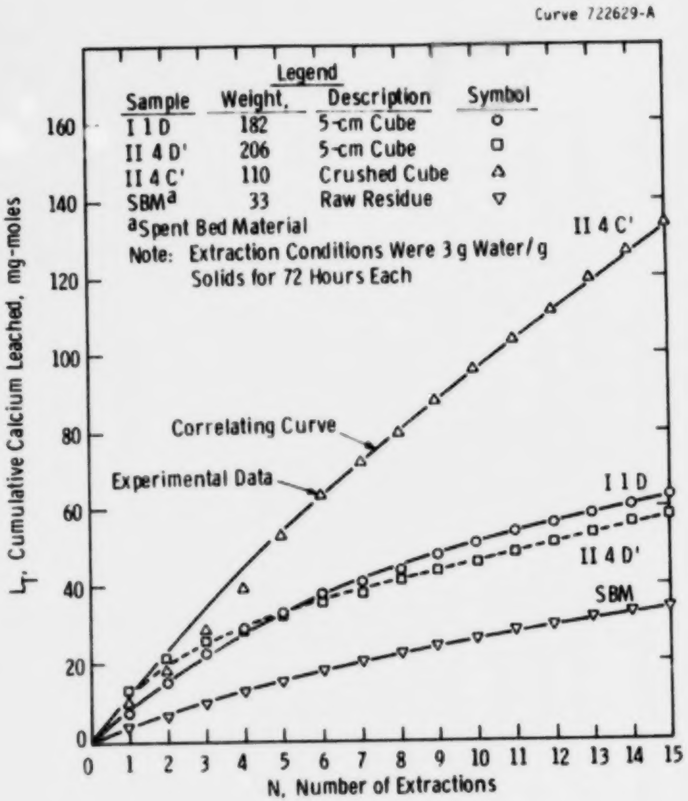


Figure 51 - Leaching of Calcium from Exxon Spent Sorbent/Carry-over Compacts

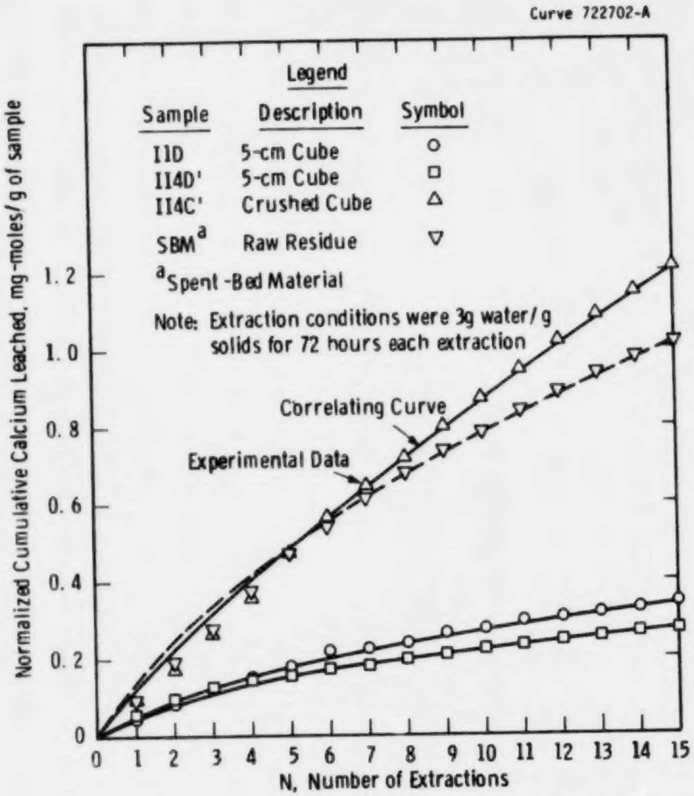


Figure 52 - Leaching of Calcium from Exxon Spent Sorbent/Carry-over - Normalized Basis

where L_T = cumulative calcium leached after N extractions, mg-moles, and L_O, b_1 and b_2 are constants. Differentiating this yields an expression for the leaching rate, mg-moles per extraction:

$$\frac{dL_T}{dN} = L_0 b_1 e^{-b_1 N} + b_2 \quad .$$

Table 69 presents numerical values for the constants for four cases. Figures 51 through 54 show that the experimental data are represented well by the empirical equations. We used a piece-wise, least-squares approach to the curve fitting which can probably be improved if desired.

Calculated Leach Rates

For comparisons we calculated rates at two different times, the initial rate and the rate at 1080 hours (15 extractions) (Table 70). Although the leach water was always three times the sample weight, the sample size was not constant, so rates were normalized by dividing by the initial sample weight to obtain specific leach rates in terms of mg-moles calcium/g of sample-hr.

With respect to initial rates, the raw spent bed material had the highest specific calcium loss rate. Forming the material into cubes reduced this rate by a factor of about 3. A longer curing time (60 vs. 7 days) was associated with a further decrease in specific leach rate. Crushing the cube to powder resulted in an increase in leach rate, but even then only to about 80 percent of that of the unprocessed material.

In all four cases specific leach rates attenuated with time, the greatest reduction occurring for II4D′, which had been cured the longest (60 days). To evaluate the long-term results further, the nature of the test material should be invoked:

1. The spent bed material (SBM) was tested as received. The original sorbent was 2380 by 707 μm (8-25 mesh).

Table 69

CONSTANTS IN THE EMPIRICAL CORRELATION OF CUMULATIVE CALCIUM LEACHED VERSUS NUMBER OF EXTRACTIONS

Sample Number	Description				Constants		
	$\frac{\text{Carry-over}}{\text{Total Solids}}$	$\frac{\text{Water}}{\text{Total Solids}}$	Curing Time, days	Form	L_0*	$-b_1$†	b_2
I1D	0.358	0.445	7	Cube	27.954	0.29718	2.266
II4D′	0.100	0.300	60	Cube	27.371	0.30930	1.934
II4C′	0.100	0.300	60	Powdered Cube	26.637	0.22848	7.113
Spent Bed Material	0.000	0.000	-	Raw Powder	11.746	0.29062	1.458

*L_0 and b_2 have the dimensions mg-moles Ca/extraction.
†b_1 is dimensionless.

2. The other three specimens were prepared from SBM that had been ground to -125 μm.
3. Specimen II4C′ was crushed to powder before being tested.

If the average particle size for SBM is taken as about 1200 μm, then the surface area per gram of material for SBM should be about 40 times that for the 5-cm cubes, yet the leach rate was only 3-to-5 times that for the cubes. This suggests that grinding the SBM may make the material

Table 70

CALCULATED LEACH RATES FOR SELECTED FBC RESIDUES

Quantity	Sample Identification			
	I1D	II4D′	II4C′	Spent Bed Material
Sample Weight, g	182	206	110	33
Leach Water, g/extraction	546	618	330	100
Sample Composition, wt %				
Spent bed material	44.4	69.2	69.2	100.0
Carry-over	24.8	7.7	7.7	--
Water	30.8	23.1	23.1	--
	100.0	100.0	100.0	100.0
Total Calcium, as Ca	11.6	15.7	15.7	21.8
Leach Rates, μg moles Ca/g sample-hr				
Initial	0.807	0.701	1.667	2.050
After 1080 hours	0.180	0.136	0.923	0.632
Leach Rates, mg moles Ca/m^2-hr				
Initial	11.75	11.56	--	--
After 1080 hours	2.62	2.24	--	--

more susceptible to leaching even in fixed form. This conclusion is further supported if one noted that the total calcium in the SBM was actually 30 to 100 percent higher than in the other three specimens.

Specimen II4C′ shows a long-term leach rate 50 percent higher than that of the raw SBM. This difference might be due to a combination of the initial grinding effect noted above plus the regrinding to powder. The particle size distribution was not measured, but if it averaged 800 μm this could account for the higher leach rate long term compared to SBM. It would not explain the lower initial rate, however, but subsequent work might show that the difference in leach rates between specimens such as II4C′ and SBM are within experimental variance.

Leaching Model

For an actual residue disposal operation, the residues may be processed to a monolithic mass. To show the advantage of such a choice, one may visualize a mass 10 m high by 100 m long by 100 m wide, which might be accumulated in one year from operation of a 200 MWe plant. We would further assume, as a first approximation, that leaching is mainly a surface phenomenon. We also assume no fissuring of the monolith. Leach rate at time t is then expressible as:

$$L_T' = \frac{dL_T}{dt} = kA \quad ,$$

where

L_T' is the leach rate in mg-moles calcium/hr,

A is the total surface exposed to leaching, m^2, and

k is a proportionality constant, mg-moles calcium/m^2-hr.

For a rectangular mass,

$$A = 2(LW + WH + LH)$$

where

L = length of the mass, m

W = width, m, and

H = height, m.

Two of these dimensions can be related to the third:

$$L = a_1W$$

$$H = a_2W$$

so that,

$$A = 2W^2(a_1 + a_2 + a_1a_2) \quad .$$

If, instead of as a monolith, the residue was deposited as N particles of uniform size, say a cube of side E, the number of particles would be

$$N = \frac{LWH}{E^3} = \frac{W^3}{E^3} a_1a_2 \quad ,$$

and the total surface area would be

$$S = 6E^2 \frac{W^3}{E^3} a_1a_2 = 6a_1a_2 \frac{W^3}{E} \quad .$$

If one compares,

$$\frac{S}{A} = \frac{3a_1a_2}{a_1+a_2+a_1a_2} \frac{W}{E} \quad .$$

If $a_1 = 1$, and $a_2 = 0.1$ to conform to the mass visualized above,

$$\frac{S}{A} = \frac{1}{4}\frac{W}{E} \quad .$$

So if $E < W/4$, the surface area will be larger for the particulate deposit than for the monolith, and the leach rate will be larger. If one assumes E = 5 cm, then S is 500 times A, and the leach rate for 5-cm cubes is 500 times that of the monolith. This illustrates the rationale for fixation of residues to monoliths.

Leach rates for granular materials appear to be more meaningful when expressed as quantity of solute leached per gram of material being leached per unit time. For masses the more meaningful rate is the quantity of solute leached per unit of surface area per unit time.

Further calculations can be made to bring out the effect of certain constraints, if we assume these operate independently. For the actual deposit we would think that the area leached by rainfall would be the top and perhaps the (four) sides, but not the bottom. We would neglect contributions due to permeability. The surface area for the monolith visualized above would be 14,000 m^2. Table 71 shows the leach rate after 1080 hours to be 2.24 mg-moles calcium/m^2-hr, yielding a rate of 4.3 kg/hr, expressed as $CaSO_4$. Presumably this rate would attenuate with time for two reasons: the surface areas would decrease, and, since the block is really not all soluble calcium, diffusional resistances would increase. If, however, we assumed no decrease in leaching rate after 1080 hours and that the mass was all $CaSO_4$, complete solution of the mass would require nearly 3500 years. For 30 years' operation, if only the solution rate were involved, the total mass produced would require 105,000 years for complete solution. A more exact estimate would take into account the fact that the area exposed to leaching is decreasing.

An average rainfall of 1.5 m/year, however, is another constraint since this corresponds to a flow of only 1.71 m^3/hr (452 gal/hr). With maximum efficiency of contacting, the concentrations of $CaSO_4$ in the two leachates would then be 2510 and 3000 ppm, respectively. The solution rate of the unfixed residue would be limited by rainfall to 5.13 mg $CaSO_4$/hr.

Still further, the actual calcium content will probably be considerably less than that for saturated $CaSO_4$. The laboratory leach data at 1080 hours suggest a concentration of perhaps only 100 mg Ca/ℓ, which is equivalent to 340 mg $CaSO_4$/ℓ, well below 10 x DWS or 250 mg/ℓ. With modest improvement this amount would be within the DWS itself. Without fixation the concentration could be six times as great, although still unsaturated and less than 10 x DWS. The corresponding solution rates with the available water would thus be 0.58 and 3.49 Mg $CaSO_4$/hr. The latter is thus set by the quantity of water available and the efficiency of contacting. The former is not governing since the effective constraint is the area available for leaching, and the rate is the 0.0043 Mg/hr calculated above. In contrast, the leaching rate for the unprocessed spent sorbent of 0.632 μg moles Ca/g-hr shown in Table 70 is equivalent to 11.2 Mg $CaSO_4$/hr, which is 2600 times that for monoliths and would result in complete solution in less than two years.

Casting small masses, as for example 5-cm cubes, is not very helpful: the time for complete solution of the 10 x 100 x 100 m quantity is about 4.5 years.

Further Constraints

The above calculations are, however, constrained further by the efficiency of contacting and, for the granular material, also by the quantity of rainfall available. If we assume that a saturated solution of $CaSO_4$ is formed (3000 ppm), complete solution of the above mass would require 4.3×10^7 m^3 of water. At an average rainfall of 1.5 m/yr in the United States, the mass would last nearly 3000 years, whether or not the residue is processed to monoliths. For 30 years' operation the total mass produced would last 90,000 years. Placing residues from large FBC plants in the environment, therefore, means making a source of substances such as $CaSO_4$ and $Ca(OH)_2$ available for leaching by environmental waters for a very long time.

The overall conclusion is that, considering the leachate production as above, if the FBC residues are placed in a landfill, the effect will be the potential generation of an average of 1.71 m^3/hr of a saturated solution of $CaSO_4$. The actual amount is expected to be very much less. In any case, it is not yet clear that this will represent an unacceptable environmental impact since, in general, there will be dilution from natural waters. Further, fixation of the residues into large masses offers the potential for reducing the rate of leaching to negligible levels.

9. ENVIRONMENTAL ASSESSMENT

Results from the laboratory-scale test data on the currently available spent bed and carry-over materials suggest that it is technically feasible to dispose of the FBC residues directly without polluting the environment. Site selection, design, and management of such disposal, based on the site-specific hydrology, geology, climate, and soil composition, are critically important to success. Processing the spent FBC material will reduce its surface area and permeability and improve the heat release and leaching properties. Process choices are available to the disposal management task, with the preferred selection dependent on environmental criteria and the economics of the acceptable options.

Pending the implementation of EPA criteria with which to assess the environmental acceptability of the disposal of FBC residues, the chemical, physical, and leaching properties of the spent FBC material are compared with DWS, with the leaching properties of natural gypsum, and with the leaching properties of residues from conventional coal-burning power plants with currently commercialized FGD processes. A preliminary comparison of the environmental impact of the disposal of FBC solid wastes and FGD sludge residues from varying processing systems is presented in Table 71 based on the up-to-date results from parallel environmental testing programs. Since the samples tested resulted from the use of different coal and sorbents, an absolute comparison may be impossible, although the available data indicate the trends are meaningful.

Table 71 shows that the physical, chemical, and leaching properties of FBC residue are superior to the nonstabilized FGD sludge with regard to disposal and are comparable to the chemically and physically stabilized FGD residue.

Table 71

Dwg. 2618C33

COMPARISON OF THE ENVIRONMENTAL IMPACT OF THE FBC AND FGD SOLID AND LIQUID WASTE DISPOSAL[a]

Process	Sample	Sorbent Type	Environmental Parameters									
			Heat Release[b,c] (spontaneous temp rise) 3 g/20 ml	Trace Metal	TDS	Total[b] Organic Carbon	pH	Calcium	Magne-sium	Sulfate	Sulfite[b]	Sulfide[b]
Pressurized FBC, Once-through	Bed material, leachate	Limestone	< 0.2°C		▩	< 30 ppm	▩	▩		▨		
Pressurized FBC, Once-through	Bed material leachate	Dolomite	< 0.2°C		▨	< 30 ppm	▩	▨		▨		
Pressurized FBC, Regenerative	Bed material leachate	Dolomite / limestone	0-3°C		▩	< 30 ppm	▩	▩		▨		▩
Atmospheric FBC, Once-through	Bed material leachate	Limestone	5 to 15°C		▩	< 30 ppm	▩	▩		▨		
Atmospheric FBC, Once-through	Carry-over material, leachate	Limestone	0-3°C	(d)	▩	< 30 ppm	▩	▩		▨		
Pressurized FBC, Once-through	Carry-over material, leachate	Limestone / dolomite	< 0.2°C	(d)	▨	< 30 ppm	▩	▨	(d)	▨		
Pressurized FBC, Once-through	Processed compacts from bed carry-over mixtures, leachate	Dolomite / limestone	< 0.2°C		▨	< 30 ppm	▩	▨		▨		
FGD	Liquor of untreated sludge	Lime / limestone		▩	▩	< 30 ppm	▩	▩	▩	▩	▩	
FGD	Liquor of oxidized sludge	Lime / limestone		▩	▩	< 30 ppm		▩	▩	▨		
FGD	Leachate of dried, untreated sludge	Lime / limestone	< 0.2°C	▩	▨	< 30 ppm	▨	▩	▩	▩		
FGD	Leachate of dried oxidized sludge	Lime	< 0.2°C	▩	▨	< 30 ppm		▨	▩	▨		
FGD	Leachate of dry stabilized sludge	Lime	< 0.2°C		▨	< 30 ppm		▨		▨		
Gypsum	Leachate	Natural	< 0.2°C		▨	< 30 ppm		▨		▨		

▩ Do not meet either the drinking water or gypsum leachate criteria

▨ Pass gypsum leachate criteria but not Drinking Water Standards

☐ Pass both drinking water and gypsum leachate criteria

(a) Based on data from currently available FBC and FGD residues
(b) No existing criteria
(c) Subjected to the specified procedures, i.e., 3 g solid added to 20 ml H_2O
(d) All except two carry-over fines pass Drinking Water Standards (total of 30 samples tested)

The work on spent sorbent processing provides a basis for choosing among alternatives to direct disposal that can result in reduced environmental impact through disposal or utilization. This work includes studies on the long-term stability of low-temperature processed compacts, on the possibility of using the residues directly as aggregate in concrete (which would result in resource recovery as well as minimizing environmental impact), and on a preliminary engineering assessment of fixation.

Several approaches to investigating long-term stability were possible, but the most relevant test was judged to be the freeze-thaw cycle. If the compacts broke down into smaller fragments on aging, freezing, hydrating, or reacting with other substances, the whole point of making them would be negated. In the processing studies we decided to pursue the option of disposing of residues in production proportions only. This meant that only one process would be required rather than one for bed material and one for carry-over.

The variables included spent sorbent source, particle size range, carry-over content, spent bed material content, and forming method. To meet the constraints of time and the quantity of test material available, we devised a sequential experimental plan. We selected isostatic pressing as the initial forming method in the expectation that compacts produced in this manner would be more likely to survive freeze-thaw testing. Failure, however, would have indicated that the concept of compact formation was probably unfeasible. Specimens made from ground spent sorbent survived for 300 cycles of freeze-thaw exposure at -18 to +40°C (0° to 40°F).

An analysis of leaching concentration and rate data over 1080 hours on unprocessed and processed compacts demonstrates the potential for significantly reducing environmental impact. The potential for reducing direct effluent concentrations to the DWS level is indicated on the basis of the preliminary analysis.

An alternative disposal method tested was utilization directly by replacing some of the sand in normal concrete with fine aggregate. Portions of the three pilot plant spent sorbents were slaked in water, blended with sintered fly ash and Portland cement, and cast into 7.6 cm x 15.2 cm cylinders. After being cured for 14 days, the cylinders demonstrated axial compressive strengths in the range 10 to 24 MPa - the low end of the range for normal concrete.

The environmental impact and spent sorbent processing test results are encouraging. A comparison of the physical, chemical, and leaching properties indicates that the disposal of FBC residue would probably not cause more negative environmental effects than the residue from a conventional coal-burning power plant with FGD systems. On the basis of the findings reported here and in previous Westinghouse reports,[5,6] we expect that disposal of FBC residue will not be an obstacle in the commercialization of the FBC process.

The spent sorbent processing studies show that alternatives are available that can offer economic, resource, and environmental advantages for the disposal of FBC residues.

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APPENDIX A

SIEVE ANALYSIS USING SINGLE SIEVES UNDER VACUUM

A single sieve (150 μm opening size) preweighed to 0.1 g was placed in an Alpine Model 200 Air-Jet Sieve (manufactured by Alpine American Corp., Natick, MA). The sample (20 g) was placed on the sieve and the whole was covered by a transparent cover. The equipment was started and the sieving under vacuum allowed to proceed to 3 min. The vacuum was at least 10 in. water pressure (below atmosphere). The amount of powder remaining on the sieve was obtained by subtracting the weight of the empty sieve from the gross weight. The above procedure was repeated with sieves of decreasing opening size until an analysis had been obtained for a 32 μm screen. For smaller opening sizes, the special adaptors supplied with the machine had to be used, as did the special etched nickel sieves. For the 20 and 10 μm opening sizes, the sample weight was approximately 2 g weighed to an accuracy of 0.001 g, and, after covering the assembly with a transparent cover, the sieving time under vacuum was 9 min. For the 5 μm opening size, the sample weight used was approximately 1 g weighed to an accuracy of 0.001 g, and the sieving time under vacuum was 9 min. In all these cases the vacuum was at least 25 in. of water below atmosphere. With all of the smaller sieves and several of the larger it was found necessary to tap the cover often with the small rubber mallet supplied. The weights of powder remaining on each screen were calculated and the results plotted as "cumulative weight percent finer than" versus "equivalent spherical diameter (microns)."

APPENDIX B

ISOSTATIC PRESSING PROCEDURE

1. Insert the blank end cap into one end of a clean, dry mold and seal with waterproof vinyl tape.
2. Place the mold assembly on the vibratory table and secure in place. Set vibration to a low level and slowly add the sorbent material to be pressed. Filling is accomplished by layering and rodding until each layer offers resistance to the tamping rod. Layering and tamping ensures better composition and release of entrapped air from the sorbent.
3. Insert the end cap with the pressure vent open. This procedure releases air being compressed by the end cap during insertion.
4. Tighten the pressure relief screw and tape as in 1.
5. Place the prepared mold in the isostatic pressure chamber, set the pressure to 138 MPag (20,000 psig), and hold for 60 seconds. (Refer to Autoclave Engineering operation manual).
6. Release the pressure gradually, remove the mold assembly from the pressure chamber, and wipe dry.
7. To remove the pressed specimen from the mold assembly, remove the pressure relief screw from the end cap, untape and remove the end cap. Carefully remove the pressed specimen.
8. After the pressed specimen has been removed from the mold assembly, place it into a water bath at 25°C for 24 hours before cutting it to the desired length with a diamond cut-off wheel.
9. Return the specimens to the water bath for 12 additional days for completion of the curing cycle.

Notes:

1. The isostatic mold assemblies must be clean and free of moisture. Water will react with the sorbent and cause early curing before pressing.
2. Air must be vented from the mold through the hole in the end cap while the filled mold assembly is capped. This ensures that no positive pressure is exerted on the inside of the mold before pressing. Failure of the mold will result.
3. Both end caps must be wrapped with waterproof vinyl tape. This prevents the isostatic pressing fluid from entering the mold assembly during pressing and contaminating the isostatic press with spent sorbent.